Resonance Theory of Catalytic Action of Transition-Metal Complexes: Isomerization of Quadricyclane to Norbornadiene Catalyzed by Metal Porphyrins

Andrei L. Tchougréeff,*[a,b] Andrei M. Tokmachev,[c] and Richard Dronskowski[d]

The theory of catalytic activity of transition-metal compounds is a fascinating problem especially if a comparison of different catalysts is necessary. The isomerization of quadricyclane (QC) to norbornadiene (NB) catalyzed by transition-metal porphyrins is a challenge and incidentally a suitable benchmark for various theories of catalysis. We analyze this process in detail using a valence bond-like scheme adjusted for the description of reaction centers containing transition-metal atoms. A qualitative explanation of contrasting catalytic behavior of Mn-phthalocyanine and Co-tetraphenylporphyrin is obtained from the analysis of the spectra of local many electron states of free catalysts and their complexes with the reactant/product. This picture is supported by the numerical analysis of potential energy profiles for the QC to NB isomerization in the presence of a catalyst performed in the effective Hamiltonian approximation. This exemplary reaction is put in a more general perspective of theories of catalytic activity of transition-metal complexes and in relation with oxygenation reactions. © 2013 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24386

Introduction

Transition-metal compounds (TMCs) exhibit catalytic activity for a wealth of chemical reactions.[1–3] They are equally important both as homogeneous and heterogeneous catalysts due to a rich variety of many-electron states which influence the chemical transformation. From the point of view of a perspective, it is in a way amazing that during decades there were only scarce attempts to construct any general theory of catalytic action based on quantum mechanics/chemistry. A Google search with terms "catalysis theory" results in a collection of "application of density functional theory to understanding of some specific cases of catalysis" rather than theory of catalysis. These are not the points of our interest. Although catalysis as a whole is a rather complex phenomenon (especially in the heterogeneous setting) involving numerous elementary steps, the transformation of reactants to products in the coordination sphere of a transition-metal ion is the key step determining the potential catalytic activity or inactivity of that or another compound. One can ask oneself whether a general theory of catalysis can be constructed at all. After all, the thinkable diversity of reactions and catalysts is immense, so what might be the common principle? We are going to show that it is possible following Einstein's motto.[4] Taking the catalysis phenomenon as it is defined in the IUPAC Gold Book: "catalyst: A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis"[5] leaves to many degrees of freedom. Even a simplest model of chemical kinetics, namely, the Arrhenius law leaves at least two possibilities: (i) increase of the rate of a reaction on account of increase of the preexponent as it is believed to be in case of "enzymatic" or "template" catalysis or (ii) decrease of the activation energy of the reaction. However, already in the textbooks

catalysis is predominantly related with the option (ii).* It is not an accident as it can be shown that at least for the simplest kinetic scheme of a catalytic reaction (Michaelis-Menten mechanism) the activation energy has to decrease.[6] An analogous conclusion can be deduced also from the results.[7–10] Thus, the quantum mechanical/quantum chemical theory must explain the change of the activation energy and according to

[a] A. L. Tchougréeff
    Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1, Aachen 52056, Germany
    E-mail: andrei.tchougreeff@ac.rwth-aachen.de
[b] A. L. Tchougréeff
    Moscow Center for Continuous Mathematical Education, Moscow, Russia
[c] A. M. Tokmachev
    NBICS Centre, NRC Kurchatov Institute, 1 Akademika Kurchatova pl., Moscow 123182, Russia
[d] R. Dronskowski
    Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1, Aachen 52056, Germany

*It may be not even written that the activation energy must decrease for catalysis to occur, but the topic is always accompanied by a picture representing two energy barriers: a higher one for the noncatalytic reaction and a lower one for the catalytic one. And that is what all the students remember; even more so when they have eventually matured to professional scientists. See, for example., Atkins, P.J., de Paula, J., Physical Chemistry, OUP; Oxford, **2009**. Another issue is the selectivity achieved by using catalysts. Of course, in the practice the problem of selectivity can be equally important. In general terms one can say, that a catalyst either selectively lowers only the desired barrier on a sophisticated surface with multiple barriers or by nonselectively and uniformly lowering all of them allows to reduce the temperature at which the process can occur and by this allows a practicing chemist to have a better usage of the selectivity through the difference of the Arrhenius factors for different possible processes. The latter, most probably happens when usual burning turns to (enzymatic) breathing in living species. However, in either case whatever reasonable analysis of selectivity must start with an adequate description of the PESs.

© 2013 Wiley Periodicals, Inc.

Andrei Tchougreeff is a Principal Scientist at the Division of Electrochemistry of the Department of Chemistry of the Lomonosov Moscow State University, and since 2008, he is also Senior Scientist at the Instutut für Anorganische Chemie Rhein-Westfälische technische Hochshcule (RWTH-Aachen Universuty), Aachen, Germany. He studied Chemistry at the MSU, Russia, where he received his Master "cum laude" in 1982. His PhD in Chemical Physics at the Karpov Institute (Moscow, Russia) defended in 1989 was devoted to the physics of conducting polymers. After postdoctoral period spent in the USA, France, and Germany in the years 1991-1995 (Cornell University, Ithaca; Universite Paris-Sud, Orsay; Max-Planck-Institute für Physik komplexer Systeme, Dresden), he rejoined the Karpov Institue as a Scientist, Senior Scientist, and Principal Scientist. Habilitated (DSc) in the year 2004. Since the year 2006, he joined the MSU. In the years 1998-2012, he organized a series of prestigeous V.A. Fock Meetings on Quantum and Computational Chemistry in Russia as well as Russian-German Hans Hellmann Symposia on Theoretical Chemistry. His main research activities are focused on the study of electronic structure of complex molecular systems with use of the group-functions approximation and on developing theoretical methods and computer codes suitable for that purpose. He is the author or co-author of over 100 research articles, which are summarized in a few reviews and in the Monograph Hybrid Methods of Molecular Modeling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Andrei Tokmachev is a leading researcher at the National Research Centre Kurchatov Institute in Moscow. In 2003, he was awarded a PhD degree from Karpov Institute working with Andrei Tchougreeff. In 2004, he joined the group of Richard Dronskowski at RWTH Aachen as an Alexander von Humboldt postdoctoral fellow. In 2006, he moved to London and worked in the group of Michael Robb at Imperial College as a Marie Curie postdoctoral fellow. In 2008, he returned to Aachen for a project on local electron states. His research ineterests focus on the development of computational methods employing local many-electron states and their applications to novel materials for nanoelectronics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Richard Dronskowski, born 1961, studied chemistry and physics in Münster and received his doctorate in Stuttgart in 1990. After a one-year stay as a scientific visitor with Roald Hoffmann, he achieved his habilitation in Dortmund in 1995. In 1996 he went to RWTH Aachen University where he is currently holding the Chair of Solid-State and Quantum Chemistry. His interests lie in synthetic solid-state chemistry, in neutron diffraction, and in the quantum chemistry of the solid state (electronic structure, magnetism, linear methods, phase prediction, thermochemistry). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the standard interface between the physical and quantum chemistries the corresponding deformation of the potential energy surface (PES) or profile of the original noncatalytic reaction to a new one occurring in the catalytic setting. The search of the required deformations can enormously profit from the classic article[11] describing geometry changes in excited states that is the deformation of the respective PESs in simple terms of the symmetries of the molecular orbitals (MOs) repopulated throughout the excitation. However, we follow here a somewhat different route.

Transition-metal porphyrins serve as efficient homogeneous catalysts for a rich variety of processes of technological importance such as oxygenation and isomerization of hydrocarbons. They are also successfully used as biomimetic models of enzymatic reactions. The experimental data show that the catalytic activity of transition-metal porphyrins strongly depends on the metal itself but can be significantly modified by peripheric substitution of the porphyrin ring and by the axial ligation. Whatever theory attempting to describe, qualitatively (and even more if quantitatively) catalytic activity of different TMCs should pay special attention to details of interactions of the catalyst and reactants at the reaction center.

The isomerization of quadricyclane (QC) to norbornadiene (NB) is an archetypical model reaction involving the rearrangement of a four-membered ring into a pair of double bonds (Fig. 1). This reaction is symmetry restricted according to the Woodward-Hoffmann rules,[12,13] as seen in a simple orbital diagram (Fig. 1).[†]

There are many experimental and theoretical studies on either isomer[18–21] as well as on the interconversion process.[22–24] The isomerization of NB to QC (inverse process) proceeds

---

[†]The system QC/NB is known as having a great potential for constructing photo-switchable molecular machines[14] and the solar energy storage.[15,16,17]
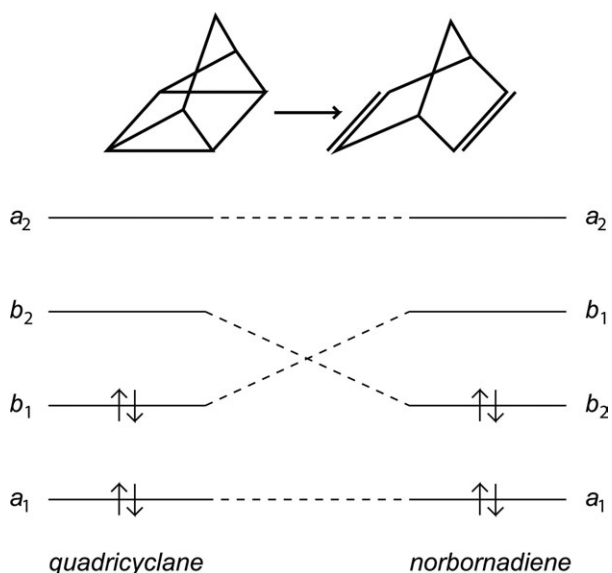
Figure 1. Scheme of isomerization of QC to NB together with the orbital crossing diagram.

photochemically, and it is established that the transformation goes through the lowest triplet state $^3A_2$.[23] This excitation promotes one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and makes the reaction photochemically allowed in the sense of the Woodward-Hoffmann theory as it is foreseen by the respective Pearson's rule.[25]

Compounds of different classes are known to catalyze this isomerization process. They include Rh(I),[26] transition-metal porphyrins,[27] Co chelates,[28] $LiCB_{11}Me_{12}$,[29] Cu(II), and Sn(II) salts.[30,31] A general explanation of catalytic action of the thermally forbidden isomerization process by metal salts is typically based on the concept of electron transfer catalysis.[32–34] It is assumed that the reaction proceeds through some negatively or positively charged intermediate. In this case, the estimated barrier is only 4.8 kcal/mol.[35] The isomerization of the QC cation to the NB cation is well studied in the literature.[36–39] The reaction path maintaining the C_{2v} symmetry implies that the highest point on the potential energy profile is a conical intersection. At the same time, the symmetry is not strictly maintained and the reaction actually proceeds through the configurations of a lower symmetry.

Despite its tentative practical importance, the catalytic transformation of QC to NB is of interest for us not by itself rather as an example of catalysis of a reaction forbidden by the Woodward–Hoffmann rules (and moreover of one, which is indeed kinetically restricted in accordance to these rules having as it is known many exceptions[40]). It was found that some transition-metal porphyrins are effective catalysts for this isomerization, whereas others do not exhibit any catalytic activity.[27,41] This "discontinous" behavior can be attributed to effects of the transition-metal d-shells. In this article, we provide an analysis of this catalytic reaction and explain difference in behavior of various transition-metal porphyrins as catalysts with respect to the above isomerization process with use of the generalized paradigm of the resonance of the valence

bond (VB) structures. Because of "perspective" character of the present article in the next Section, we review some previous attempts performed in this direction. After that, we briefly describe the effective Hamiltonian-based implementation of the generalized VB approach to the chemical transformations in the coordination sphere of TMCs. The results of its application to the catalytic isomerization of QC to NB constitute the following Section. Finally, we draw some conclusions with respect to the mechanism of the catalytic process under consideration and put it in the relation with the latest theoretical considerations in the area of the metaloxo enzymes.

Perspectives I. Earlier Theories

Previous attempts to explain the experimental data on catalytic activity of transition-metal porphyrins in the QC to NB isomerization reduce to two different mechanisms of catalytic action. The first one is similar to the electron-hole catalysis as introduced by Wolkenstein[42,43] and is known as the Mango-Schachtschneider (MS) theory of catalysis.[44] This theory exploits the MO picture of molecular electronic structure. In its framework, a formal explanation of catalysis of symmetry forbidden reactions is given. It is based on the assumption that in the presence of a catalyst the orbital symmetry is conserved due to transfer of two electrons from the HOMO of the reactant to a virtual orbital of the catalyst of the same symmetry with simultaneous transfer of two electrons from an occupied orbital of the catalyst on the LUMO of the reactant. It makes the isomerization allowed according to the Woodward-Hoffmann rules.

Although the MS theory looks quite reasonable (despite the reservations concerning the applicability of the Woodward-Hoffmann rules in general[40] and the necessity of changing the states of *four* electrons when moving along the reaction coordinate), the comparison of catalytic activity of different complexes in its framework leads to serious contradictions with experimental data. Already in 1970, Manassen had shown[41] that the MS theory gives incorrect results when used to describe contrasting catalytic activity of Co-tetraphenylporphyrin (CoTPP) and Mn-phthalocyanine (MnPc) in the QC to NB isomerization. The simplest description of the ground state of CoTPP is the single determinant doublet $^2A_{1g}$ with doubly filled d_{xz} and d_{yz} orbitals (see Fig. 2), which are of the same symmetry as the "crossing" molecular orbitals of the reactant (b_1 and b_2).

Therefore, CoTPP is unable to take electrons from the reactant and can not exhibit any catalytic activity according to the MS theory. At the same time, the same orbitals in Mn are only singly filled and could in principle participate in redistribution of electrons between the catalyst and the reactant which is (in a line with the MS theory although not precisely following its details) a condition for exhibiting catalytic activity. The experimental situation is precisely inverse: CoTPP exhibits remarkably catalytic activity while MnPc is not active at all.

The vibronic theory of catalysis belongs to the earliest attempts of constructing a general theory of catalysis.[45] According to it, a catalyst modifies the electronic structure of reactants like in the Wolkenstein's and MS approaches assisting
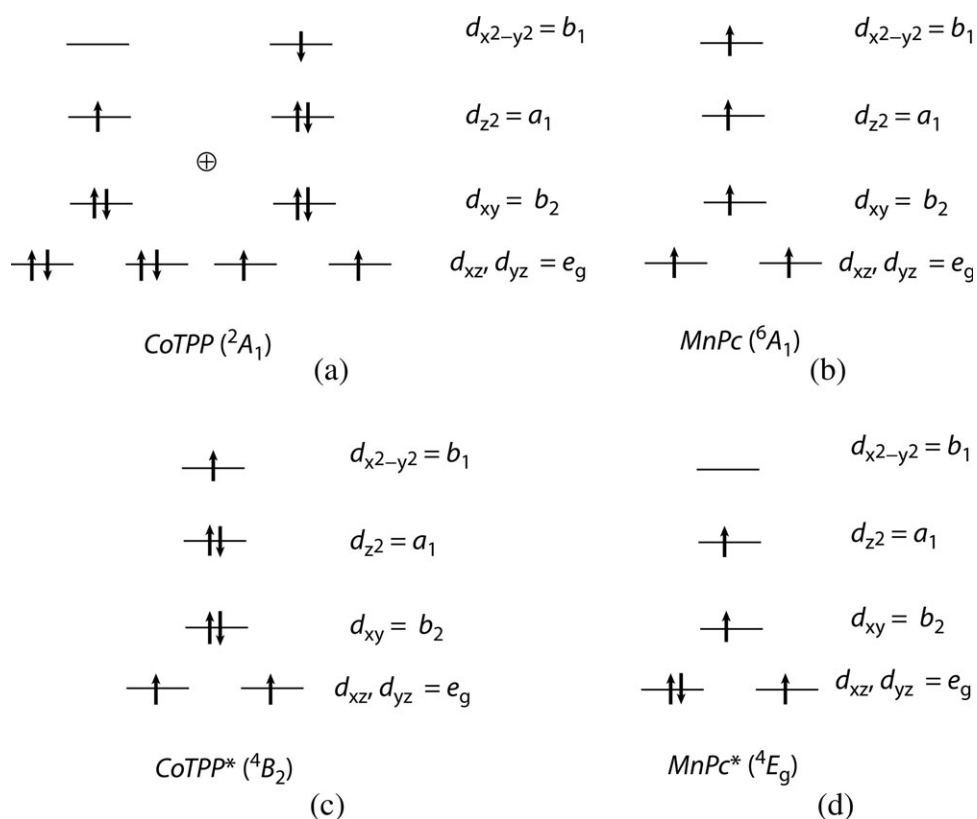
$d_{x2-y2} = b_1$

$d_{z2} = a_1$

$\oplus$

$d_{xy} = b_2$

$d_{xz}, d_{yz} = e_g$

CoTPP ($^2A_1$)

(a)

$d_{x2-y2} = b_1$

$d_{z2} = a_1$

$d_{xy} = b_2$

$d_{xz}, d_{yz} = e_g$

MnPc ($^6A_1$)

(b)

$d_{x2-y2} = b_1$

$d_{z2} = a_1$

$d_{xy} = b_2$

$d_{xz}, d_{yz} = e_g$

CoTPP* ($^4B_2$)

(c)

$d_{x2-y2} = b_1$

$d_{z2} = a_1$

$d_{xy} = b_2$

$d_{xz}, d_{yz} = e_g$

MnPc* (^4E_g)

(d)

Figure 2. Dominant configurations contributing ground and lowest excited states of considered metal-porphyrins. Symmetry notation is given with respect to the group C_{4v}. (a) Ground state of the catalytically active CoTPP. Symbol '$\oplus$' refers to a mixing (*resonance*) of the configurations with some amplitudes by no means equal. (b) First excited state of the catalytically active CoTPP. (c) Ground state of the catalytically inactive MnPc. (d) First excited state of the catalytically inactive MnPc.

in the redistribution of electronic density between the MOs of the reactants (either occupied or empty in the free reactants) with the mediation of the orbitals of the catalyst in a way similarly to the Dewar-Chatt-Duncanson's donation/back-donation.[46] This modifies the reactants' energy profile which is quantified by the orbital vibronic constants—in fact by the slopes of the coordinate dependence of the corresponding orbital energies depicted by crossing dashed lines in Figure 1—of the repopulated orbitals, which in turn are the key quantities of the vibronic theory. The amounts of the densities redistributed between the reactant's MOs are to be found from a calculation of the complex of the catalyst with reactants/products (the catalytic complex—CC). In this sense, the vibronic theory is "reactant-centered": it describes a tentative catalytic action in terms of the reactants' vibronic constants, leaving the properties of a TMC important for its tentative catalytic activity out of focus.

The vibronic theory encounters problems analogous to the MS theory trying to account for the nature of the transition metal in the catalyst. Like in the MS theory, the metal orbitals which could be used to mediate the required redistribution are available in the catalytically inactive MnPc and are not available in the catalytically active CoTPP. This brought us some time ago to a more general formulation of the problem of catalysis as of one of the deformation of the entire PES of free reactants/products through their interaction with a cata-

lyst occurring when the reactants' become coordinated to the catalyst. Recognizing the quantum-mechanical nature of the processes involving the catalyst and the reactants allows for a natural description of the PES of catalytic transformation in terms of those of the various quantum states of the components of the catalytic complex (CC). Indeed, taking a CC as one formed by the free reactants and the free catalyst allows us to take the products of the corresponding electronic states as a suitable basis for describing the CC which justifies terming it as a "resonance theory of catalysis."[6,47–50]‡ This provides a necessary formal point of view upon the problem.[4] The catalytic action is a significant modification of the PES leading to a lowering of the activation barrier. It takes place due to admixture of configurations, where catalyst and reactant are

---

‡It must be understood that by the free catalyst we understand here not the original species added to the reaction pot to make the reaction to run faster (this latter more deserves the name of precursor) but that composition of the central atom and ancillary ligands which actually turns out to be a part of the CC. This of course complicates the treatment since the real composition and even more the structure of the free catalyst thus defined are largely unknown. This predefines particular importance of the catalysts which presumably are not very different from their respective precursors. Namely, those possessing rigid chelating ligands (see below) may be thought not to change too much then the respective CC's are formed. With this assumption one may also think that the electronic states of the precursor-similar free catalysts can be taken as those of the precursors themselves.

simultaneously excited, to the unperturbed ground state, provided the excited state of the reactants has at least a smaller barrier on its PES along the reaction path.

The role of a catalyst in this theory is postulated to populate the reactive excited state of the reactant/product. The very idea of such a population is by no means new (see e.g., Ref. [51] where catalysis had been explained by thermal population of the reactive state). The question is where the energy required for populating the excited states is going to come from. In the present article, we test a particular quantum-mechanical mechanism of populating the reactive state through the formation of an entangled state—one which under all circumstances cannot be represented as a product (antisymmetrized) of the electronic states—of the catalyst and reactants.[52] The necessary energy is then the energy of formation of chemical bond between the reactants and the catalyst: the resonance energy.

Now we are about to apply these ideas to analyze the catalytic transformation of QC to NB. In order to undertake such a study, one must possess a good model of the PES of transformation of free reactants to free products. Although a purely qualitative picture in this case is fairly provided by the Woodward-Hoffmann rules[12,13] even semiquantitative estimates are not possible in this framework. The models of required quality can be constructed in the framework of the valence-bond theory as suggested by Shaik.[53,54] However, transformation of QC to NB which involves breaking and formation of two bonds requires for its description too many resonance structures which makes the valence-bond picture too complicated. Thus we combined earlier ideas[40] of describing the chemical reactivity with use of linear combinations of resonating electronic configurations whatever they are with an even earlier idea[55] to supply an explicit consideration of electrons in the π-electron chromophore with a harmonic potential describing the effect of all other electrons and nuclei widely used in later works.[56,57] This has been formalized in Ref. [6,47–50] by considering the dependence of the orbital energies of b_1- and b_2-orbitals assumed to have the simplest possible linear form:

$$\epsilon_{b_1} = k_{b_1}(q - q^{\neq}), \epsilon_{b_2} = -k_{b_2}(q - q^{\neq}) \qquad (1)$$

where $q^{\neq}$ stands for a point on the reaction coordinate q where the b_1- and b_2-orbital energies are equal as shown in Figure 1. The slopes k_{b_1} and k_{b_2} are precisely the orbital vibronic constants required by the theory.[45] The effect of all other electrons and nuclei is assumed to be covered by a harmonic potential $K(q - q_0)^2/2$ added to the energy. The energy profiles of the QC (reactant) and NB (product) which can be obtained with the respective single determinants are shown on the left panel of Figure 3. The intersecting parabolae fairly represent the diabatic states required by the VB theory of reactivity.[53,54]§
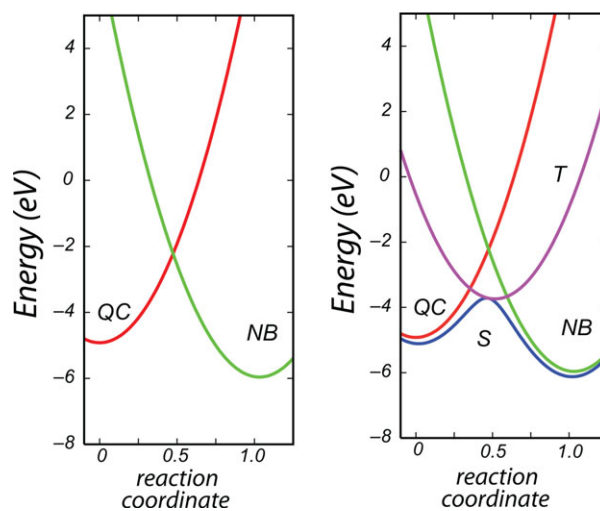

Figure 3. Diabatic and adiabatic terms for the transformation of QC to NB. Color coding (visible online): red and green, respectively, the energy profiles for the single determinant states representing QC and NB as shown in Figure 1. Blue and magenta are singlet (ground) and triplet (excited) adiabatic energy profiles respectively for the thermal and photochemical transformation of QC to NB. Zero energy level is chosen arbitrarily although other parameters are adjusted to reproduce the experimental heat of reaction and its activation barrier.[49] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

By taking the electron-electron interaction in its simplest form, the one-center (Hubbard–Anderson) repulsion (for more details see[49]) of the magnitude γ, we determine another important component of the valence-bond theory of reactivity,[53,54] namely, the resonance energy stabilizing the linear combination of the diabatic states. Some algebra (namely, solving a square equation) shows that the stabilized linear combination of the reactant and product diabatic states (the singlet adiabatic ground state of the system QC/NB) has the energy:

$$E_S(q) = B(q) - \sqrt{(k_{b_1} + k_{b_2})^2(q - q^{\neq})^2 + \gamma^2/16} \qquad (2)$$

where

$$B(q) = (k_{b_1} - k_{b_2})(q - q^{\neq}) + \gamma/4 + K(q - q_0)^2/2$$

so that the resonance energy is $\gamma/4$. It is depicted in the right panel of Figure 3 where one can easily recognize the minima corresponding to QC and NB that are not that much different from the diabatic/single determinant minima and the fact that the resonance stabilization occurs in the vicinity of the crossing of the adiabatic terms. The single-excited configurations give rise to the adiabatic triplet state of QC/NB with the energy:

$$E_T(q) = B(q) - \gamma/4 \qquad (3)$$

which is as well depicted in Figure 3. A remarkable feature of the present model is that in the intersection point $q^{\neq}$ of the orbital energies the energy profiles of the many-electron states $^1A_1(=S)$ and $^3A_2(=T)$ touch each other. Although it is not true in reality, this does not prevent a cautious usage of the model in the present study.

---

§Those who are familiar with the VB theory of reactivity[53,54] immediately recognize the fact that promotion energy of the reactant G_r is its excitation energy to the state corresponding to the reaction product (notice that this is a double! excitation). Also, the energy at the intersection point fairly represents the fraction of the promotion energy fG_r serving as the bare activation energy for the diabatic states.

With these prerequisites, we can start dealing with the catalytic process. As already mentioned, a configuration basis set suitable for considering the modification of the energy profile under the coordination with the tentative catalyst are the (antisymmetrized) products of the states of the catalyst and the reactants/products. The simplest (two-level) model is spanned by two such products. In the case of CoTPP, its ground state $^2A_{1g}$ multiplied by the $^1A_1$ state of QC produces the wave function Ψ_{gg} (gg stands for two ground states) having $^2A_1$ symmetry (we go here to the lowest nontrivial symmetry group of the CC which is the C_{2v} symmetry). The orbital diagram of this state is shown in Figure 4a.

The energy profile of this state is the S one of Eq. (2) which are depicted as S and "S," respectively in Figures 3 and 5.

It is visually clear that an admixture of the configuration Ψ_{ee} (ee stands for two excited state multipliers) which has the same energy profile as the triplet Eq. (3) shifted by the energy ΔE_C of the $^4B_{2g}$ state, to the Ψ_{gg} configuration is going to damp the activation barrier relative to that of the adiabatic

Figure 5. Energy terms relevant to description of the catalytic transformation of QC to NB within the two-level model. Color coding for the 'S' and 'T' profiles is the same as in Figure 3. Cyan is used for the profile CC of the transformation within the CC as given by the model Eq. (4). Zero energy level is chosen to be that of the ground state of the free catalyst. Quotation marks are used to stress that it goes about the profiles of the QC to NB transformation in the coordination sphere of a catalyst but with the interaction turned off. Having QN/NB coordinated results in the the catalyst energy gap ΔE_C to be the minimal energy separation between the 'S' and 'T' terms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

energy profile of the free QC/NB system. Therefore, the trial wave function of the form:

$$\Psi = \Psi_{gg} \cos\phi + \Psi_{ee} \sin\phi, \qquad (4)$$

where the weight of the "reactive" state Ψ_{ee} ($\sin^2\phi$) with the triplet QC state as a multiplier determines the catalytic activity being an example of an "entangled" state[52] is rich enough to reproduce the key features of the intraspheric transformation.

One can make sure that both configurations involved in Eq. (4) have the same total spin and spatial symmetry as in the spectroscopic notation they are both the $^3A_2$ states.¶ This is a prerequisite for having a nonvanishing matrix element of the
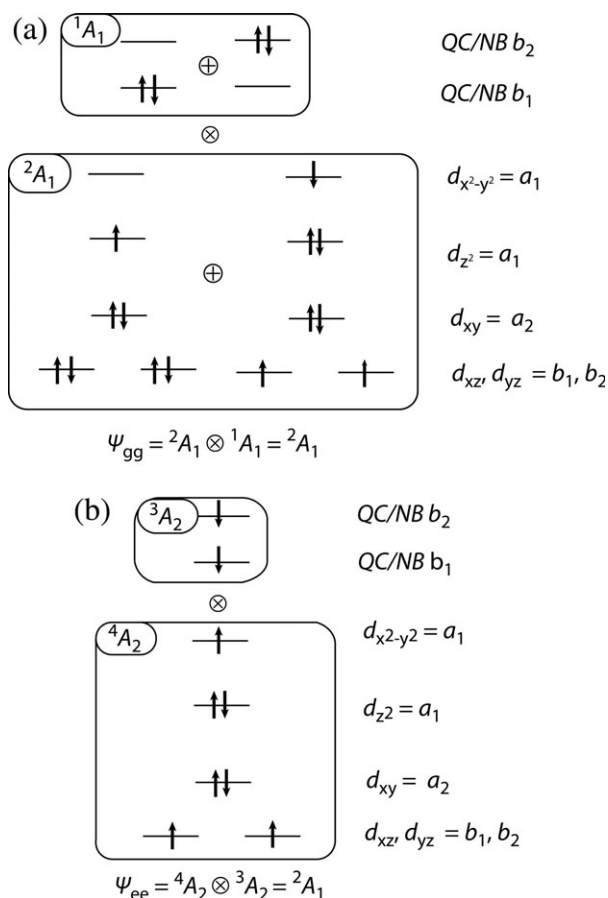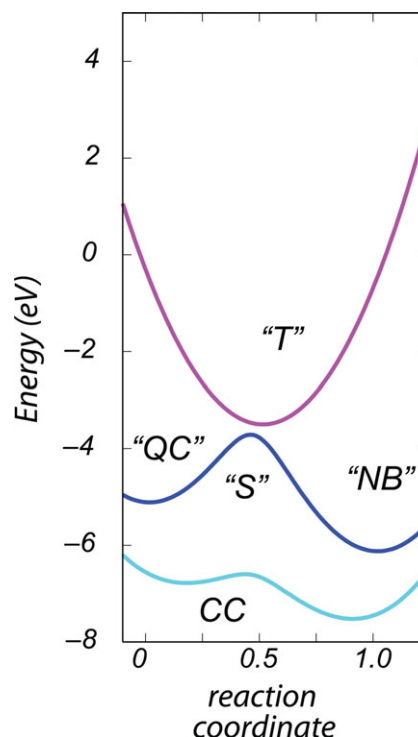

Figure 4. Orbital diagrams for the basis states of the two-states model Eq. (4). Symmetry notation is given relative to the C_{2v} point group. The symbols '⊕' and '⊗' are used to denote, respectively, a linear combination of the electronic states with more or less aritrary amplitudes (resonance) and the antisymmetrized product of the electronic states of the respective subsystems. (a) The pictorial representation of the Ψ_{gg} state - the product of ground states of the catalyst (CoP) and QC/NB. (b) The pictorial representation of the Ψ_{ee} state - the product of excited states of the catalyst (CoP) and QC/NB.

¶The general form of the spin- and symmetry-based selection rules allowing to restrict otherwise "unlimited variety of possibilities" [4] is:

$$|S_C^g - S_R^g| \leq S \leq S_C^g + S_R^g$$
$$5 \quad |S_C^e - S_R^e| \leq S \leq S_C^e + S_R^e \qquad (5)$$
$$\Gamma = \Gamma_C^e \otimes \Gamma_R^e = \Gamma_C^g \otimes \Gamma_R^g$$

The spin and irreducible representation symbols (S and Γ) without subscript and superscripts refer to the CC and must be the same for the configurations Ψ_{gg} and Ψ_{ee} for they could interact; the subscripts R and C refer to the reactants and catalyst respectively, the superscripts g and e refer to the ground and excited states.

Hamiltonian $g = \langle \Psi_{gg}|H|\Psi_{ee}\rangle \neq 0$ necessary to make the above linear combination/entanglement nontrivial. If the latter is the case, finding the approximate ground state energy of the CC is equivalent to solving another square equation stemming from the eigenvalue problem for the q-dependent 2×2 matrix:

$$\begin{pmatrix} E_S(q) & g \\ g & E_T(q) + \Delta E_C \end{pmatrix}$$

representing the effective Hamiltonian of the CC in the subspace spanned by the pair of configurations Ψ_{gg} and Ψ_{ee}. In the point $q^{\neq}$ where the orbitals and diabatic states of QC/NB cross and the adiabatic states of the free QC/NB touch each other ($E_S(q^{\neq}) = E_T(q^{\neq})$) the energy of the lowest adiabatic state of the CC has the form:

$$E_{S,T}(q^{\neq}) + \frac{\Delta E_C}{2} - \sqrt{\frac{\Delta E_C^2}{4} + g^2} \approx \begin{cases} E_{S,T}(q^{\neq}) - \frac{g^2}{\Delta E_C} & \text{for } g \ll \Delta E_C \\ E_{S,T}(q^{\neq}) + \frac{\Delta E_C}{2} - g & \text{for } g \gg \Delta E_C \end{cases}$$

so that the flattening of the activation barrier relative to that on the adiabatic energy profile $E_S(q)$ of the free QC/NB amounts in two limits to

$$\Delta\Delta E^{\neq} = \begin{cases} -\frac{g^2}{\Delta E_C} & \text{for } g \ll \Delta E_C \\ \frac{\Delta E_C}{2} - g & \text{for } g \gg \Delta E_C \end{cases}$$

This situation is depicted in Figure 5 for a reasonable constant value of the effective interaction g. The catalytic action through the resonance (entanglement) of the states Ψ_{gg} and Ψ_{ee} is obvious. In order to take into account the more general situation when two adiabatic energy profiles of the reactants/products do not touch each other at $q^{\neq}$, but remain separated by an energy gap $\Delta E_R = E_T(q^{\neq}) - E_S(q^{\neq})$ the above result must be modified: the gap ΔE_R must be added to ΔE_C:

$$\Delta\Delta E^{\neq} = \begin{cases} -\frac{g^2}{\Delta E_C + \Delta E_R} & \text{for } g \ll \Delta E_C + \Delta E_R \\ \frac{\Delta E_C + \Delta E_R}{2} - g & \text{for } g \gg \Delta E_C + \Delta E_R \end{cases} \tag{6}$$

The formula Eq. (6) shifts the perspective of the theoretical treatment of catalysis in a profitable direction: from exclusively reactants/products to the catalyst but without loosing the reactants from sight. In a way, the result is trivial: the consequences of setting reactants in interaction with catalyst depend on the energy spectra of two interacting systems (ΔE_C and ΔE_R) and on the interaction energy (g). However, it allows for a complete qualitative analysis of what might happen when a reactant is put in a contact with a tentative catalyst. If the ground state adiabatic energy surface of reactants/products with a high activation barrier is always separated from any reactive state (with small or no barrier) by a considerable energy gap ($\Delta E_R \gg g$) nothing is going to help: it is not possible to improve such a reaction with use of any catalyst. If, however, an accessible reactive state of the reactants/products can be identified, tentative catalysts can be further sought on the basis of the spectrum of their electronic states and their suitability for interaction. The excited states of a tentative catalyst must be of low energy as well (in the estimate enters the sum of two excitation energies) which

explains the activity of transition-metal complexes as a whole class: these species basically have low-lying excited states in their d-shells. However, having low-lying excitation of suitable spin and symmetry is not a universal property of all TMCs. Specificity of their individual spectra allows to explain the drastic differences in the catalytic activity of similar compounds of different transition metals. The reason is that in a series of transition-metal ions the changes in the number of d-electrons occurs in a discrete manner, so that the spectra of the ions of the same degree of oxidation may differ very strongly. In our exemplary case of CoTPP versus MnPc, the energy of the first excited states satisfying the selection rules Eq. (5) are respectively 0.21 and more than 2 eV (see for details[47–49]) which immediately explains the difference in their activity observed in experiment.[41]

The proposed scheme is capable to trace also tiny distinctions within the series of catalysts/reactants differing, for example, by chemical substitution distant to the reaction center. Within such series one can observe correlations between catalytic activity either with respect to a series of similar substrates or to a series of similar catalysts and some spectral characteristics of either of them. In the series of similar catalysts or reactants, the excitation energies (respectively ΔE_C and ΔE_R) change depending on distant substituents, and this produces correlation between the variations of the activation energy (catalytic activity) and the outcome of the methods probing these excitations (the larger the excitation energies, the worse are the prospects for improving the reactivity by the catalyst).

Finally, the interaction strength (i.e., actual magnitude of g) is an indispensable component of the entire picture. In the literature, this important issue frequently escapes the attention. Even if the symmetry allows some interaction to be nonvanishing, it is its actual magnitude which enters Eq. (6) and determines the amount of the lowering of the activation barrier. It is not enough only to single out appropriate catalyst states on the basis of symmetry: it is a preliminary step. One has to be sure that the found states indeed interact strongly enough so that the activation energy noticeably lowers. This brings us to the question of the physical nature of the interaction assuring the magnitude of the matrix element g of the order of about 1 eV.**

Considering an important role of open-shell complexes as well as our above result on importance of combining the

---

**In a way, the same question arises in the frame of the general scheme of the reactivity analysis along the lines.[53,54] What is the physical nature of interaction which assures appearance of the resonance matrix element B between the diabatic reactant and product states which has the required magnitude? In the specific case of the QC to NB isomerization considered in the present paper it was the two electron Coulomb interaction which was capable to mix the states differing by excitation of two electrons without breaking the Slater rules, but is it possible to find a suitable interaction—that is, one giving the matrix element of a magnitude conforming to experiment and not breaking the Slater rules in all cases of intersection of the reactant and product adiabatic states? And does it mean that a transformation must proceed as a multi-step process involving one or more intermediates if for a pair or reactant/product diabatic states one cannot find a suitable interaction, for example, in the cases when the ground state of the product is more than doubly excited state (differs by more than two spin-orbitals) of the reactant?

singlet and triplet state of QC/NB can easily bring to a conclusion of a spin-orbital nature of g. The importance of a spin-orbital interaction for catalysis by transition-metal complexes is frequently mentioned in the literature (see the review[58]) particularly in relation with catalysis of the spin-forbidden reactions (we return to this issue later). Nevertheless, the bare spin-orbital interaction in a transition-metal ion, which lies on the 0.1 eV scale, hardly produces a matrix element of about 1 eV which is necessary to transform an energy profile with a barrier of about 1.5 eV (that of the thermal isomerization of QC to NB) into an almost barrierless one as occurring in the ligand sphere of CoTPP.

This is in a way the same question as that of the energy supply for populating a reactive excited state. Our conjecture is that the energy comes from the chemical bonding, that is, electron hopping between the catalyst and reactants/products. For this end in the present article, we apply a somewhat more general model taking into account a larger number of configurations produced by simultaneous excitations of catalyst and reactant and/or by electron transfers between them.[††]

Methodic Development

The theoretical description of a catalytic process requires a detailed knowledge of the electronic structure of the catalytic complex (CC). In the case of catalysis by TMCs, the problem turns very complicated because not only the interaction between catalyst and reactant is not trivial, but the electronic structure of free TMCs themselves requires a fairly subtle description. The ground and excited states of many TMCs require essentially multiconfigurational wave functions.

Catalytic systems based on TMCs are typically polyatomic molecular systems. Nevertheless, a detailed account of electron correlations is necessary only for relatively small parts of them. This is a prerequisite for applying hybrid methods,[59,60] where different parts of the system are described by using electronic wave functions of different form. If the electronic structure of a TMC alone is to be described, a statically correlated treatment is necessary for the d-shell, while the rest can be calculated using a simpler one-electron approximation. This concept is a basis for the Effective Hamiltonian Crystal Field (EHCF) method[61] which has been thoroughly tested.[62–65] In this method, the trial wave function is taken in the form

$$\Psi = \Phi_d \otimes \Phi_l, \tag{7}$$

where Φ_d and Φ_l are wave functions for electrons in the d-shell and in the ligands, respectively; the symbol $\otimes$ has to be understood as an antisymmetrized product of the wave functions of the electrons in two subsystems. The electronic variables of the subsystems are separated using the effective Hamiltonian approach based on concerted usage of the Löwdin partitioning technique and the McWeeny group-functions theory.[66,67] That simple setting, however, does not prevent the EHCF method from being capable to reproduce extremely subtle features of electronic structure of TMC's like spin crossover transitions in quasioctahedral complexes of Fe(II) and Co(II)[65,68] and the ^3E ground state of Fe(II) porphyrin[64] which represents a serious problem even for very advanced methods of ab $initio$ quantum chemistry.

Although the EHCF method is a natural framework for analysis of electronic structure of TMCs, its formulation is in many aspects restrictive. It does not allow for treatment of catalytic processes because (i) the one-electron approximation is not suitable for description of electron reorganizations both in the d-shell and in the the ligands undergoing transformation (reactive ligands) and (ii) interactions between reactive (rather than spectator) ligands and the d-shell are not trivial and include mixture of different combinations of their electronic states. Thus, the EHCF method had been recently generalized for numerical analysis of chemical transformations in the coordination sphere of TMCs.[69] In this setting, the subsystem which requires a nontrivially correlated description (the reaction center) is formed by the d-shell of the transition-metal ion and by several molecular orbitals repopulated throughout the transformation process (r-subsystem). The rest can be treated in a simpler manner not involving too much correlation. The wave function of a CC is then assumed to be given by the antisymmetrized product:

$$\Psi = \Phi_{d \oplus r} \otimes \Phi_{l \ominus r}. \tag{8}$$

Of course, the wave function of the CC of the form Eq. (8)—like that of the form Eq. (7) for the usual transition metal complex—can be only approximate due to interactions which entangle—see below—the electronic states of the parts of these molecules. Like the EHCF method had been derived for the usual transition metal complexes by separating (i.e., desentangling) the variables referring to the d-shell and the ligands through a concerted usage of the Löwdin and McWeeny approaches[66,67] the effective Hamiltonian method for the many-electron wave function of the form Eq. (8) with the electronic variables divided between two subsystems: reaction center hereinafter denoted as $d \oplus r$ and spectator subsystem denoted as $l \ominus r$ have been consructed by the same techniques and practically implemented for the CNDO, INDO, and MINDO/3 semiempirical Hamiltonians for the $l \ominus r$-subsystem.[69] More details on the methods used can be found in review[59] and monograph[60] although specific of application to the problem of catalysis is highlighted elsewhere.[69,70]

Along the lines of the EHCF method,[61] the wave function $\Phi_{d \oplus r}$ of the reaction center has to be taken as a full configuration interaction (CI) wave function in the configuration basis of

---

[††]This situation calls for a kind of explanation in more general terms. Apparently, the model Eq. (4) of the CC ground state is a correlated (multiconfigurational, multireference) model. The correlations explicitly taken into account by this model can be fairly described as static due to the mentioned multireference character of the trial wave function. At the same time, the matrix element g is a result of effective admixture of many other configurations. In this sense it is correlation as well, but it can be fairly called dynamical correlation since it manifests itself in the value of the parameter (effective matrix element) g, so to say in the forces acting in the system. It is the same kind of dynamical correlation which manifests itself in the magnitude of the effective exchange parameters of the spin-Hamiltonian description of conjugated π-electronic systems; that effectively accounting the charge transfer states.

the $d \oplus r$ subspace. However, in order to simplify the analysis it can be equivalently rewritten through the complete sets of the eigenstates of the d-shell and the r-subsystem: [6,50]

$$\Phi_{d \oplus r} = \sum_{k,i} A_{ki} \Phi_d^k \otimes \Phi_r^i. \tag{9}$$

Generally, in the state of a reaction center described by the wave function $\Phi_{d \oplus r}$ [Eq. (9)] the electronic states of the reactants and the catalyst (its d-shell) are "entangled". Under this assumption we obtain the electronic energy of the CC:

$$E = \langle \Psi | \mathbf{H} | \Psi \rangle = \sum_{k,i} (A_{ki})^2 (E_d^k + E_r^i) +$$
$$+ \sum_{k,i} \sum_{k',i'} A_{ki} A_{k'i'} \langle \Phi_d^k \otimes \Phi_r^i | \mathbf{H}_{int} | \Phi_d^{k'} \otimes \Phi_r^{i'} \rangle. \tag{10}$$

The above equation generalizes the two-level model Eq. (4) by formally adding to it all possible configurations of the reactants/products and the catalyst. The interaction operator H_{int} includes all possible interactions between the catalyst and reactants, that is, the electron hopping between the d- and r-subsystems and the Coulomb interactions between electrons in these subsystems. The choice of the r-subsystem in this reaction is natural - these are the molecular orbitals (MOs) of the b_1 and b_2 symmetries. These two orbitals with two electrons in them represent the simplest choice of the r-subsystem adequate for our analysis. All other electrons (the $l \ominus r$-subsystem) are decribed on the semiempirical self consistent field (SCF) level. The electron correlation in the r-subsystem is taken into account when we use the full CI method for the $d \oplus r$-subsystem.

Calculations and a New Model

Following our general methodology to identify the effect of a catalyst, we have to compare an energy profile describing a reaction without a catalyst with one in the ligand sphere of a catalyst. In order to obtain a profile of a noncatalytic reaction we used the semiempirical MINDO/3 Hamiltonian which is known to reproduce correctly the heats of formation of "organic" systems.[‡‡] The SCF-based procedure is adequate in the vicinity of the QC or NB minima but it clearly fails in the vicinity of the intersection of the diabatic terms. Following our general theoretical consideration, it is logical to complement our calculations by configuration interaction within the "crossing" MOs of the b_1 and b_2 symmetries.

Figure 6. Energy profiles for isomerization reaction without a catalyst (upper curve) and with CoP as a catalyst (lower curve) for the CC configuration shown in Figure. 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 represents the energy profile for the QC to NB isomerization as obtained from these (SCF/CI-MINDO/3) calculations. The border points of the reaction path (0 and 1) correspond to the QC isomer with the C–C distances 1.54 and 1.46 Å in the ring and to the NB isomer with the corresponding C–C distances, respectively, of 1.34 and 2.564 Å as corresponding to the experimental geometries in the clathrates. These distances are set to be linear functions of the reaction coordinate. All other coordinates are optimized for each point on the reaction path. The minima on the energy profile do not correspond to the points 0 and 1 on the reaction path since the MINDO/3 method reproduces the experimental spatial structures not perfectly. This all produced the barrier of about 50 kcal/mol which we consider to be an acceptable starting value for further semiquantitative estimates, as we are interested in the fact of the deformation of the profile, not in the exact barrier value.

Next, we considered the isomerization process in the coordination sphere of the cobalt porphyrin (CoP) as a potential catalyst. The EHCF method correctly reproduces the d-d spectra of transition metal porphyrins.[62,64] We made two further structural assumptions (see Fig. 7): (i) the distance between the catalyst and the center of the four-member ring of QC (transforming into two double bonds of NB) r_{Co-ctr} remains constant and (ii) the catalyst conserves its structure during the isomerization. The setting of the CC near the reactant and the product geometry is depicted in Figure 7.

Our calculations show that the wave function Ψ_{gg} in Eq. (4) with the components depicted in Figure 4 is indeed the main component of the ground state of the CC for the values of r_{Co-ctr} larger than 1.98 Å. Tracking this state along the reaction path we found that the total weight of configurations with electron transfers between d- and r-subsystems in either direction is always smaller than 1% and the weight of the Ψ_{ee} configuration with two excited wave functions for the d- and r-subsystems is less than 0.5%. Such a small admixture of the reactive configurations does not provide any significant lowering of the activation barrier (smaller than 0.5 kcal/mol). Even in

---

[‡‡]Semiempirical SCF calculations show that in the case of NB the energy difference between the ground singlet state ($^1A_1$) and the excited triplet state ($^3A_2$) is about 7 eV. Although this value is twice as large as the experimental one[18] it reproduces the fundamental feature that these states are energetically well separated. In the narrow range near the barrier of the ground state transformation the triplet state even becomes energetically favorable as compared to the singlet state. However, this inversion takes place only for very small segment of the reaction path (less than 3% of its entire length) and the relative stabilization of the triplet does not exceed a few kcal/mol, thus this feature cannot be responsible for lowering of the barrier by many dozens of kcal/mol (see below).
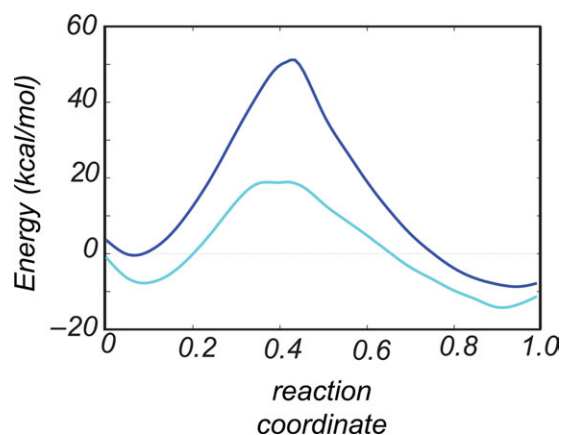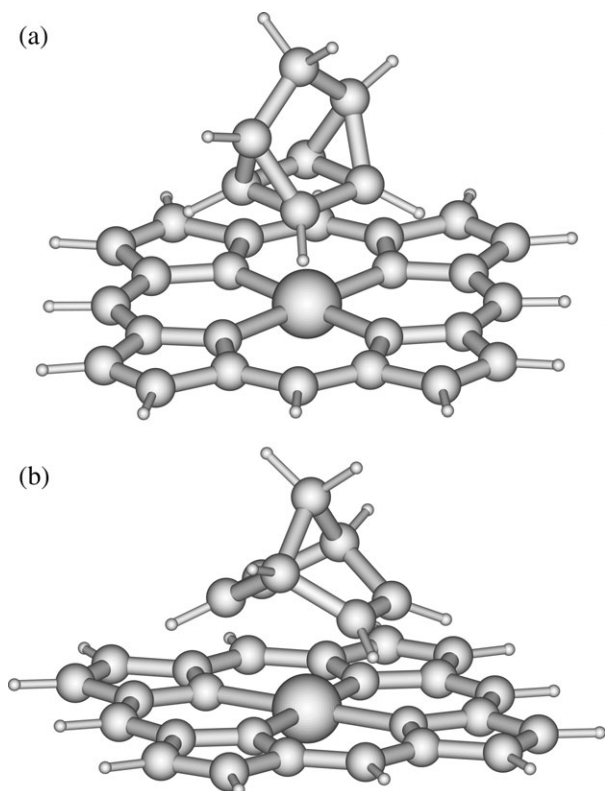
(a)

(b)

Figure 7. Catalytic complex of Co-porphyrin with QC/NB used in calculations. Geometries (a) and (b) are shown close to the ends of the reaction path. Different perspective views are used in (a) and (b) for better visibility.

the range of geometries where the Ψ_{gg} state becomes excited the admixture of configurations with electron transfer or with simultaneous excitations of the catalyst and QC/NB remains small.

When the QC/NB unit further closes to the metal porphyrin unit, different states in the d-shell of CoTPP nonuniformly shift on the energy scale and the ground state of the CC changes due to change of the ground state of the catalyst. The doublet state with the configuration shown in Figure 8 becomes the ground state. These doublet states stem from the ^2E_g state of the free catalyst which lies only by 0.35 eV higher than its $^2A_{1g}$ ground state. This degenerate state splits into the B_1 and B_2 components since the symmetry of the CC reduces to C_{2v}. That qualitatively explains the involvement of this state in the catalytic action upon isomerization. Indeed, the configuration formed by the antisymmetrized product of the $^2B_2$ component of the state of the d-shell and the singlet configuration $^1A_1$ of QC can effectively mix with the configuration formed by the $^2B_1$ state of the d-shell and the $^3A_2$ state of QC. In the case of NB the situation is the same but our calculations show that the roles of the components $^2B_1$ and $^2B_2$ become interchanged. Namely, the configuration formed by the product of the $^2B_1$ component of the state of the d-shell and the singlet configuration $^1A_1$ of NB mixes with the configuration formed by the $^2B_2$ component of the state of the d-shell and the $^3A_2$ triplet of NB. The relevant orbital diagrams are shown in Figure 8.

If the symmetry of the CC had been exactly C_{2v} it would lead to the crossing of the terms $^2B_2$ and $^2B_1$ of the CC so that the catalytic process would be symmetry forbidden in a strict sense, not by the Woodward-Hoffmann rules. However, this symmetry is only approximate since the small motions of the reactants relative to the catalyst (e.g., rotations around the second order axis—that one going through the metal center and the apical carbon atom of the QC/NB moiety transversal to the porphyrin ring so that the relative rotations of the moieties around it remove the reflections in the mirror planes of the C_{2v} group) can further reduce it and allow for an effective mixing of these terms. One has to notice, however, that the catalytic activity in the sense accepted in the present article (the deformation of the energy profile reducing the barrier) is achieved in the two $^2B_2$ and $^2B_1$ states of the CC due to entanglement with the reactive $^3A_2$ triplet of QC/NB. It is not important how weak the symmetry reducing interaction mixing the $^2B_2$ and $^2B_1$ states is, the potential barrier is already reduced.

Numerical analysis of the process of intraspheric reorganization of QC to NB at $r_{Co-ctr} = 1.75$ Å shows that the ground state of the CC contains the $^2B_2$ and $^2B_1$ components of the splitted ^2E_g state of the catalyst for the major part of the reaction path. It also contains an admixture of different configurations with a noticeable but never dominating weight of those with electron transfers between the d-shell and r-subsystem (in fact the charge transfer states contribute about 18% for the cationic form of QC/NB and 4% for the anionic form for geometries close to the barrier). In the range close to the barrier, the weight of configurations containing the triplet state of QC/NB as a multiplier increases up to 60%. The situation can be also described by a four-state model spanned by the configurations Ψ_{gg}, Ψ_{ee}, Ψ'_{gg}, and Ψ'_{ee} taken as the products of the $^2B_2$ and $^2B_1$ states of the catalyst and the $^1A_1$ and $^3A_2$ states of QC/NB as depicted in Figure 8. The energy profile of the isomerization in the presence of CoTPP is given in Figure 6. It can be seen that the significant lowering of the barrier (by about 25 kcal/mol) indeed occurs in this case.

The results obtained have been verified by extending the r-subsystem by adding one more occupied and one more unoccupied orbital of QC/NB to it. By doing so, the r-subsystem of the four orbitals a_1, b_1, b_2, and a_2 and four electrons was considered. Our calculations show that the results are stable with respect to this modification of the model. Although the total weight of configurations where the a_1 orbital is not doubly occupied and/or the a_2 orbital is not vacant is not vanishingly small (about 4% near the barrier) it does not lead to any significant modification of the entire picture: the weight of electron transfer configurations increases only by 0.008 (mostly due to increase of the weight of the cationic form of QC/NB) but the barrier further lowers by only 0.3 kcal/mol.

When MnPc is tested for tentative catalytic activity with use of the above technique, it shows that the change of the electronic state does not occur and admixture of configurations with electron transfers or excitations of the catalyst and QC/NB is vanishingly small for all reasonable geometries. This can be understood on the basis of analysis of the electronic spectrum of the tentative catalyst: the lowest excited state of MnP
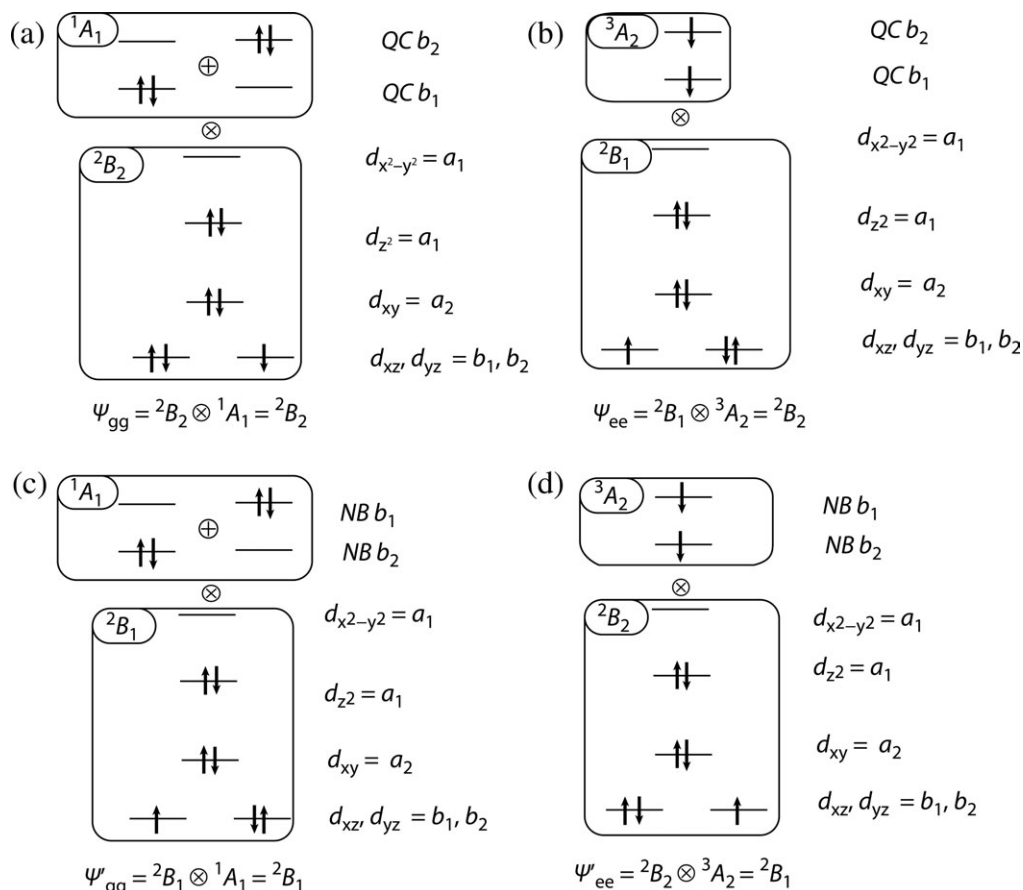
Figure 8. Orbital diagrams for the dominant contributions to the ground state of the extended model Eq. (9) accroding to our calculation with CoP as tentative catalyst at $r_{Co-ctr} = 1.75$ Å. Like in Figure 4 symmetry notation is given relative to the C_{2v} point group. The symbols '⊕' and '⊗' are used to denote, respectively, a linear combination of the electronic states with more or less aritrary amplitudes (resonance) and the antisymmetrized product of the electronic states of the respective subsystems; (a) and (c) give the pictorial representations of the Ψ_{gg} and Ψ'_{gg} states - the products of the components ($^2B_2$ and $^2B_1$) of the splitted ^2E_g state of the catalyst (CoP) and the ground $^1A_1$ state of QC/NB; (b) and (d) give the pictorial representations of the Ψ_{ee} and Ψ'_{ee} the products of the states $^2B_2$ and $^2B_1$ of the catalyst (CoP) and of the excited state $^3A_2$ of QC/NB.

(^4E_g) lies about 2 eV higher than the ground state ($^6A_{1g}$) and any potential mechanism of activation is not going to work. The transfers of electron pairs which are thought to be a source of catalytic activity in the MS theory[44] are energetically very unfavorable. The same, however, applies to the potential population of excited states in the reactant and the d-shell. Indeed, when calculated at $r_{Mn-ctr} = 1.75$ Å the lowering of the barrier of the QC to NB isomerization is smaller than 1 kcal/mol. Our consideration thus supports the experimental finding on the inactivity of MnPc in this reaction as well as the conclusions based on the simple two-level model.

Conclusions and Perspectives II

The QC to NB isomerization is an experimentally well studied archetype of symmetry (Woodward-Hoffmann) restricted reactions. The explanation of contrasting catalytic activity of different transition-metal porphyrins in this reaction is a good benchmark for theories of catalysis. The qualitative picture of catalytic activity described in the present paper can serve as an exemplary demonstration of applying the ideas of resonance of different electronic configurations for describing the

catalytic activity of transition metal complexes. Our analysis allowed to propose a new mechanism of catalytic action of CoTPP. It includes a change of the ground state of the catalyst due to variations of the ligand field induced by the reactants. This factor is not trivial and significantly enriches our previous more simplistic view upon this process as given by the two-state model. Our considerations are supported by reaction energy profiles with and without the catalyst calculated using a specially designed hybrid quantum chemical method.[69] Our analysis of reaction in the coordination sphere of MnPc supports the conclusion concerning the reasons of its inactivity in this isomerization.

It is worth saying that the proposed VB-based approach first of all applies as an analysis tool indicating "where to watch" when dealing with (transition metal complex) catalysis either experimentally or with use of standard numerical techniques. If a reliable numerical procedure is available one can most probably use any type VB "reading" of the wave function[71] to establish what configurations contribute to the ground state at hand. The important difference from such a usage already reported in the literature in relation to organometallic reactivity[72] is the proposed by us "shift of the focus," namely

describing the CC in terms of entangled states of the catalyst and reactants/products. On the other hand, our results indicate a tentative demand for namely a VB-based computational tool for catalysis, since, as we have shown above, the relevant wave function has only relatively small contribution of the states with the charge transfer between the catalyst and reactants, whereas the single determinant approximate ground states, as it is well known, tend to overestimate their weight, by this masking the role of the respective local (catalyst *vs.* reactants/products) excitations. That is not talking about the fundamental faults of the single determinant based MS and vibronic theories (see above) which implies that the one-electron picture even of the reactive system is inadequate not talking about the description of catalytic processes; thus many-electron wave functions must be considered.

Of course, at the present time our description is incomplete. One may, however, easily figure out immediate further moves to be done: the effect of the axial ligands which may have an important influence upon the spectrum of the metal-porphyrin *d*-shell and thus change considerably the selection of its low-energy states available for formation of the entangled states must be explored. Also, lowering the symmetry of the CC from the C_{2v} accepted in the present work will be helpful for substantiating the four-level model (description in terms of the configuration space spanned by the functions Ψ_{gg}, Ψ_{ee}, Ψ'_{gg}, and Ψ'_{ee} depicted in Fig. 8).

Turning back to a perspective view of our specific example we notice that the interaction between the basis configurations either in the original simplistic two-state model or in a tentatively more realistic four-states model can be seen as an effective antiferromagnetic (that yielding the lowest possible total spin of the CC) exchange coupling between the spin of the triplet reactive state of the QC/NB and that of a suitable open shell state of the catalyst. In the two-state model, the suitable state turned out to be a quartet state which with necessary modifications fairly corresponds to the recent ideas ascribing particular importance to the high-spin states and to the intra-molecular ferromagnetic exchange (that responsible for the Hund's rule in free atoms and ions) in shaping the reactivity of metal-oxo enzymes.[73] Our calculations indicate that the situation is probably not that simple. From our point of view, the case[73] is one of the nonreactive high-spin ground state (triplet oxygen) and of the reactive low-spin (singlet oxygen) excited state. Corresponding energy profiles of the oxygenation an organic substrate are presented in Figure 9.

One can easily see that an attempt to bring together the triplet oxygen atom and a singlet organic species (both are in respective ground states) leads to the excited state of the product. By contrast, the excited singlet oxygen atom forms a bound ground state of the oxygenation product. These terms intersect somewhere and, according to the general scheme of the VB analysis, the energy at the intersection point provides an estimate of the activation energy of the thermal reaction as a fraction of the excitation energy of the oxygen atom. They correspond to different values of total spin, and the reaction is forbidden according to the famous Wigner-Witmer spin-selection rule.[76] The latter circumstance is in a way misleading, as
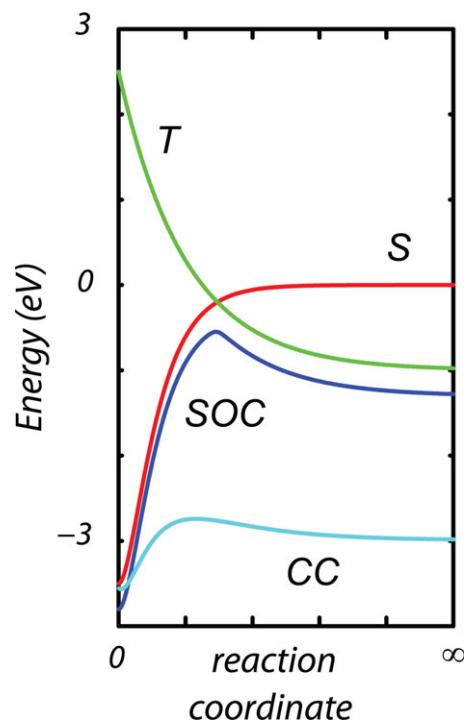

Figure 9. Schematic energy profiles for various versions of oxygenation of an organic reactant. The zero energy level is that of the separated organic species and the singlet oxygen atom. The ∞ sign denote an infinite separation of the oxygen atom and organic reactant. The profile of the oxygenation by the ground state triplet oxygen atom is sketched by the term *T* (green). The profile of the abstraction of the singlet oxygen atom is sketched by the term *S* (red). Bringing the triplet oxygen atom from infinity to a contact with an organic species leads to the excited state of the oxospecies which explains the decaying character of the *T* term. By contrast, bringing the excited singlet oxygen atom in contact with an organic species in its ground (singlet) state results in the bound term *S*. Turning on a weak interaction (like the spin-orbit coupling) yields an adiabatic profile sketched as *SOC* (blue; the curve is arbitrarily shifted down as a whole to ensure visibility, otherwise it visually coincides with the respective segments of the *T* and *S* terms) which although refers to a process formally allowed by the spin-conservation rules has a barrier of the order of excitation energies of either oxospecies or oxygen atom.[74,75] Strong (resonance or effective exchage interaction) yields as strongly deformed profile sketched as *CC* (cyan) with the barrier diminished according to the magnitude of the interaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

it may suggest that overcoming the spin restriction is the main task of an oxygenation catalyst or enzyme.[58] It is true that the spin-orbit coupling may remove the spin restriction and convert the intersecting energy profiles into an adiabatic profile leading to the singlet product. Nonetheless, it is too weak and cannot significantly reduce the barrier height as shown in Figure 9. Thus the *fact* that the barriers in the enzymatic or biomimetic oxygenation processes taking place at room temperature are low remains unexplained. If one, by contrast, assumes the strong resonance interaction (effective exchange, donation/back-donation) between the catalyst and the oxygen atom one obtains an energy profile with a barrier reduction according to Eq. (6), which may be well strong. Obviously, the existence of high-spin states of the tentative catalyst is a precondition for formation of the entangled state of the CC containing the singlet and the triplet states of the oxygen atom

as required even by our simplistic two-level model. In that sense, our resonance theory of catalytic action agrees with the conclusions derived from analysis of numerical studies.[73] The situation considered in the present article is inverted with respect to that in the oxygenation. In the QC/NB transformation one deals with the nonreactive low-spin state which has to be modified through the formation of an entangled state with the reactive high-spin state. It turns out that the states of the catalyst required by the selection rules in order to form necessary entangled states are not necessarily high-spin and that the high-spin by itself does not guarantee high catalytic activity with respect to all reactions. One can only state less categorically that different types of transformations require different TMCs as catalysts. Of course, it would be of great interest to address the oxygenation processes within the proposed resonance paradigm in more depth in order to elucidate the factors controlling the catalytic activity of various metal complexes as functions of the metal nature, its oxidation state, and details of coordination. Although the developed program implementation of the resonance approach to catalysis is semiquantitative since it employs an approximate Hamiltonian and relies up on semiempirical parameters it can be useful for obtaining simple and cheap estimates of variations of PESs up on coordination to tentative transition metal complex catalysts. A more rigorous nonempirical implementation of the resonance theory of catalysis is feasible. It will be a close relative of the CASSCF and CASPT2 methods with a special emphasis on the choice of the active spaces and the detail of the procedure used for separation of electronic variables. A hybrid QM/MM formulation is as well possible and well desirable in the context of enzymatic catalysis.

Acknowledgments

[1] A. Nakamura, M. Tsutsui, Principles and Applications of Homogeneous Catalysis; Wiley-Interscience: New York, **1980**.

[2] C. Masters, Homogeneous Transition-Metal Catalysis; Chapman and Hall: London, **1981**.

[3] B. Meunier, *Chem. Rev.* **1992**, *92* 1411.

[4] A. Einstein, *Science* **1940**, *91*, 487.

[5] IUPAC Compendium of Chemical Terminology, 2nd ed (the 'Gold Book'); A. D. McNaught, A. Wilkinson, Eds.; Blackwell Scientific Publications: Oxford, **1997**.

[6] A. L. Tchougréeff, *Int. J. Quantum Chem.* **1996**, *58*, 67.

[7] C. Amatore, A. Jutand, *J. Organomet. Chem.* **1999**, *576*, 254.

[8] S. Kozhukh, S. Shaik, *J. Phys. Chem. A* **2008**, *112*, 6032.

[9] S. Kozhukh, S. Shaik, *Acc. Chem. Res.* **2011**, *44*, 101.

[10] A. Uhe, S. Kozhukh, S. Shaik, *J. Comp. Chem.* **2011**, *32*, 978.

[11] R. Hoffmann, *Pure Appl. Chem.* **1970**, *24*, 567.

[12] R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.* **1965**, *87*, 395.

[13] (a) R. B. Woodward, R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781; (b) R.B. Woodward, R. Hoffmann, Die Erhaltung der Orbitalsymmetrie; Verlag Chemie: Weinheim, **1970**; (c) R.B. Woodward, R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press: New York, **1970**.

[14] R. Herges, T. Winkler, *Eur. J. Org. Chem.* **2001**, 4419.

[15] T. Nishikubo, A. Kameyama, K. Kishi, T. Kawashime, *Macromolecules* **1992**, *25*, 4469.

[16] V. A. Bren, A. D. Dubonosov, V. I. Minkin, V. A. Chernoivanov, *Rus. Chem. Rev.* **1991**, *60*, 451.

[17] A. D. Dubonosov, V. A. Bren, V. A. Chernoivanov, *Rus. Chem. Rev.* **2002**, *71*, 917.

[18] B. O. Roos, M. Merchán, R. McDiarmid, X. Xing, *J. Am. Chem. Soc.* **1994**, *116*, 5927.

[19] A. M. Helms, R. A. Caldwell, *J. Amer. Chem. Soc.* **1995**, *117*, 358.

[20] H. Mackenzie-Ross, M. J. Brunger, F. Wang, W. Adcock, T. Maddern, L. Campbell, W. R. Newell, I. E. McCarthy, E. Weigold, B. Appelbe, D. A. Winkler, *J. Phys. Chem. A* **2002**, *106*, 9573.

[21] D. G. Lishan, K. V. Reddy, G. S. Hammond, J. E. Leonard, *J. Phys. Chem.* **1988**, *92*, 656.

[22] R. D. Bach, I. L. Schilke, H. B. Schlegel, *J. Org. Chem.* **1996**, *61*, 4845.

[23] A. Cuppoletti, J. P. Dinnocenzo, J. L. Goodman, I. R. Gould, *J. Phys. Chem. A* **1999**, *103*, 11253.

[24] M. Rosi A. Sgamellotti, F. Franceschi, C. Floriani, *Inorg. Chem.* **1999**, *38*, 1520.

[25] R. G. Pearson, Symmetry Rules for Chemical Reactions: Orbital Topology and Elementary Processes; Wiley: NY, **1976**.

[26] H. Hogeveen, B. J. Nusse, *Tetrahedron Lett.* **1973**, 3667.

[27] K. S. Bishop, III, *Chem. Rev.* **1976**, *76*, 461.

[28] D. Wöhrle, P. Buttner, *Polym. Bull.* **1985**, *13*, 57.

[29] S. Moss, B. T. King, A. de Meijere, S. I. Kozhushkov, P. E. Eaton, *J. Michl, Org. Lett.* **2001**, *3*, 2375.

[30] E. C. C. Chuang, K. C. Lin, *J. Phys. Chem. B* **2002**, *106*, 132.

[31] T. L. Fan, H. F. Chin, K. C. Lin, *J. Phys. Chem. B* **2004**, *108*, 9364.

[32] N. J. Saettel, J. Oxgaard, O. Wiest, *Eur. J. Org. Chem.* **2001**, 1429.

[33] T. Clark, In Electron transfer II, Topics in Current Chemistry; J. Mattay, Ed.; Springer: Berlin, **1996**, *177*, 1.

[34] T. E. Shubina, T. Clark, *Z. Naturforschung B* **2010**, *65*, 347.

[35] K. Ishiguro, I. V. Khudyakov, P. F. McGarry, N. J. Turro, H. D. Roth, *J. Am. Chem. Soc.* **1994**, *116*, 6933.

[36] T. Clark, *Acta Chem. Scand.* **1997**, *51*, 646.

[37] Y. Inadomi, K. Morihashi, O. Kikuchi, *J. Mol. Struct. (Theochem)*, **1998**, *434*, 59.

[38] P. E. Larsson, N. Salhi-Benachenhou, X. C. Dong, S. Lunell, *Int. J. Quantum Chem.* **2002**, *90*, 1388.

[39] P. E. Larsson, N. Salhi-Benachenhou, S. Lunell, *Chem. Eur. J.* **2004**, *10*, 681.

[40] N. D. Epiotis, Theory of Organic Reactions (Reactivity and Structure); Springer-Verlag: Berlin-Heidelberg-New York, **1978**.

[41] J. Manassen, *J. Catal.* **1970**, *18*, 38.

[42] Th. Wolkenstein, The Electronic Theory of Catalysis on Semiconductors; Pergamon Press: Oxford, **1963**.

[43] Th. Wolkenstein, *Adv. Catal.* **1973**, *23*, 157.

[44] F. D. Mango, *Adv. Catal.* **1969**, *20*, 291.

[45] (a) I. B. Bersuker, *Zh. Fiz. Khim.* **1985**, *59*, 1099 (in Russian); (b) I. B. Bersuker, Electronic Structure and Properties of Transition Metal Compounds: Introduction to Theory; Wiley: NY, **1996**.

[46] (a) M. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C79; (b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.

[47] A. L. Tchougréeff, I. A. Misurkin, *DAN USSR*, **1986**, *291*, 1177 (in Russian).

[48] A. L. Tchougréeff, I. A. Misurkin, *Theor. Exp. Chem.* **1988**, *24*, 398 (in Russian).

[49] A. L. Tchougréeff, I. A. Misurkin, *Chem. Phys.* **1989**, *133*, 77.

[50] A. L. Tchougréeff, *Int. J. Quantum Chem.* **1996**, *57*, 413.

[51] F. Seitz, In Advances in Catalysis and Related Subjects; W. G. Frankenburg, V. I. Komarewsky, E. K. Rideal, Eds., Academic Press: New York, **1950**;*2,* 1.

[52] K. Blum, Density Matrix Theory and Applications; Plenum Press: New York and London, **1981**.

[53] S. S. Shaik, *J. Am. Chem. Soc.* **1981**, *103,* 3692.

[54] S. Shaik, P. C. Hiberty, A Chemist's Guide to Valence Bond Theory; Wiley: NY, **2007**.

[55] J. E. Lennard-Jones, *Proc. Roy. Soc. A* **1937**, *158,* 280.

[56] A. Warshel, M. Levitt, *J. Mol. Biol.* **1976**, *103,* 227.

[57] A. Warshel, Computer Modeling of Chemical Reactions in Enzymes and Solutions; Wiley: NY, **1991**.

[58] B. F. Minaev, H. Ågren, *Collect. Czech. Chem. Commun.* **1995**, *60,* 339.

[59] A. L. Tchougréeff, A. M. Tokmachev, In Advanced Topics in Theoretical Chemical Physics; J. Maruani, R. Lefebvre, E. Brändas, Eds.; Kluwer: Dordrecht, **2003**; pp. 207.

[60] A. L. Tchougréeff, Hybrid Methods of Molecular Modeling; Springer, **2008**.

[61] A. V. Soudackov, A. L. Tchougréeff, I. A. Misurkin, *Theor. Chim. Acta* **1992**, *83,* 389.

[62] A. V. Soudackov, A. L. Tchougréeff, I. A. Misurkin, *Int. J. Quantum Chem.* **1996**, *58,* 161.

[63] A. V. Soudackov, A. L. Tchougréeff, I. A. Misurkin, *Zh. Fiz. Khim.* **1994**, *68,* 1256 (in Russian).

[64] A. M. Tokmachev, A. L. Tchougréeff, *Chem. Phys. Rep.* **1999**, *18,* 163.

[65] M. B. Darkhovskii, A. L. Tchougréeff, *J. Phys. Chem. A* **2004**, *108,* 6351.

[66] P.-O. Löwdin, *J. Math. Phys.* **1962**, *3,* 969.

[67] R. McWeeny. Methods of Molecular Quantum Mechanics, 2nd ed.; Academic Press: London, **1992**.

[68] M. B. Darkhovskii, A. L. Tchougréeff, In Recent Advances in Theory of Chemical and Physical Systems; J.-P. Julien, J. Maruani, E. Brändas, Eds.; Kluwer: Dordrecht, **2006**; pp. 451.

[69] (a) A. M. Tokmachev, A. L. Tchougréeff, I. A. Misurkin, *Int. J. Quantum Chem.* **2001**, *84,* 99; (b) A. M. Tokmachev, A. L. Tchougréeff, *Zh. Fiz. Khim. 74,* **2000**, 66 [in Russian]; (c) A.M. Tokmachev, A.L. Tchougreeff, *Russ. J. Phys. Chem. 74,* **2000**, 58 [in English].

[70] A. M. Tokmachev, A. L. Tchougréeff, *J. Solid State Chem. 176,* **2003**, 633.

[71] (a) G. Trinquier, J.-P. Malrieu, I. Garcia-Cuesta, *J. Am. Chem. Soc. 113,* **1991**, 6465; (b) C. Angeli, J.-P. Malrieu, *J. Phys. Chem. A 112,* **2008**, 11481.

[72] S. Shaik, H. Chen, *J. Biol. Inorg. Chem. 16,* **2011**, 841.

[73] S. Shaik, H. Chen, D. Janardaran, *Nature Chem.* **2010**, *3,* 19.

[74] (a) S. Shaik, A. Shurki, *Angew. Chem. Int. Ed.* **1999**, *38,* 586; (b) S. Shaik, P. C. Hiberty, *Rev. Comput. Chem.; (c) K. B. Lipkowitz, T. R. Cundari, Eds. Wiley-VCH: New York,* **2004**, *20,* 1.

[75] W. Lai, C. Li, H. Chen, S, Shaik, *Angew. Chem. Int. Ed.* **2012**, *51,* 5556.

[76] E. Wigner, E. E. Witmer, *Z. Phys.* **1928**, *51,* 859.