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THEORETICAL ANALYSIS OF CATALYTIC ACTIVITY OF TRANSITION METAL COMPLEXES IN SYMMETRY FORBIDDEN REACTIONS

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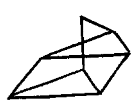
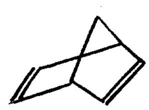
The mechanism of the catalytic activity of transition metal complexes is discussed in terms of an effective Hamiltonian of a reactant–catalyst system. The potential energy surface has been constructed for the reaction of catalytic isomerization of quadricyclane to nonbornadiene. The properties of the catalyst are found to affect strongly the activation energy of the reaction.

1. Introduction

An important problem in the field of organic synthesis and homogeneous catalysis is the elucidation of the nature of catalytic activity of metal complexes in various reactions. As an example we consider the reaction of isomerization of quadricyclane (I) to norbornadiene (II) [1–4]:



I



II

This symmetry-forbidden $2\pi+2\pi$ reaction is encountered in different variants and seems to be studied most thoroughly from the viewpoint of experiment. Catalysis of this reaction by different transition metal complexes has been studied and interpreted [2] within the framework of the Mango–Schachtschneider (MS) theory [5].

The MS approach to the explanation of catalytic activity of different complexes leads to serious difficulties pointed out in ref. [2]. The combined system (RM) of a reacting molecule (R) coordinated to a catalyst (M) conserves the orbital symmetry while transforming from the initial to the final state due to a redistribution of electrons in the system. The difficulties of the MS approach occur in an attempt to explain the catalytic activity of the complexes CoTPP (cobalt tetraphenylporphyrin) and MnPc (manganese phthalocyanin) in the isomerization of quadricyclane to norbornadiene. The orbitals d_{xz}, d_{yz} of CoTPP which have the same symmetry as intersecting orbitals of reacting moiety are fully occupied [6] and cannot accept electrons from these orbitals.

At the same time, each of the orbitals d_{xz}, d_{yz} in MnPc is singly occupied [6] and can take part in redistribution of electrons among the orbitals of the reagent. In this case the requirements of the MS theory are fulfilled and complexes of Mn(II) should display catalytic activity, in contradiction to the experiment [2].

The effect of the catalyst on the reagents is due to some type of interaction, which populates the excited (and/or ionized) states of both reagents and catalyst. The main questions are the nature of this interaction and the relationship between catalytic activity and other physical properties of the catalyst. We demonstrate in the present paper that the interaction which removes the symmetry restriction is the resonance one. This resonance interaction cannot be accounted for without using a large number of non-traditionally built configurations. Namely, we construct the configurations of the RM system as direct products $|R^0M^0\rangle$, $|R^+M^-\rangle$, $|R^-M^+\rangle$, $|R^*M^*\rangle$ of the reagent states $|R^0\rangle$, $|R^*\rangle$ and $|R^{\pm}\rangle$ and the catalyst states $|M^0\rangle$, $|M^*\rangle$ and $|M^{\pm}\rangle$. Here the upper indices denote the ground (0), the excited (*), the anionic (−), and the cationic (+) states of subsystems R and M.

A theory which intends to describe catalytic processes and interpret other properties of transition

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metal complexes should take into account the configuration interaction; this has been pointed out, e.g., in ref. [7]. We consider the resonance interaction in the framework of the Van Vleck effective Hamiltonian method. The representation of the many-electron function of RM as a sum of product of states of the subsystems R and M would allow the utilization of available experimental information on energies and symmetry properties of the electronic states of the catalyst and reagent, as do the methods of "atoms-in-molecules" or "molecules-in-molecules".

2. Model potential energy surfaces for the izomerization of quadricyclane to norbornadiene

Let us consider a simple model of the reaction: the electronic structure of a reacting system is determined by four electrons (these are the four π electrons of II, or the four electrons of the cyclobutane ring of I located on the four atomic orbitals (AOs) of the carbon atoms). The remaining electrons and the nuclei are taken into account via the elasticity parameters of the core. Now we derive the adiabatic terms (potential energy surface (PES)) of the system depending only on two parameters, i.e. change in the length (x) and width (y) of the cyclobutane ring, which we assume to retain a rectangular shape in the course of the reaction (fig. 1). In the MO LCAO approximation (molecular orbitals as linear combinations of atomic orbitals) the form of the MO is determined by the symmetry (C_{2v}) of the system:

$$|a_1\rangle = \tfrac{1}{2}(|1\rangle + |2\rangle + |3\rangle + |4\rangle)\,,$$

$$|a_2\rangle = \tfrac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle)\,,$$

$$|b_1\rangle = \tfrac{1}{2}(|1\rangle - |2\rangle - |3\rangle + |4\rangle)\,,$$

$$|b_2\rangle = \tfrac{1}{2}(|1\rangle + |2\rangle - |3\rangle - |4\rangle)\,,$$

where MOs having the symmetries A_1, A_2, B_1, B_2 are expressed via the AOs of the atoms 1–4 (fig. 1). A diagram of the energy levels (MOs) for the states of the systems I and II is shown in fig. 1. For the initial state (I) $\mathscr{E}(b_1) < \mathscr{E}(b_2)$, for the final state (II) $\mathscr{E}(b_1) > \mathscr{E}(b_2)$. The intersection of the MO levels of different symmetry in the course of the reaction I→II is a characteristic feature of a symmetry-forbidden reaction (according to the Woodward–Hoffman rules [8]).

Let us assume the Hamiltonian of the reacting system (I and II) to have the form

$$H_R = H_R^{el} + \tfrac{1}{2}K_1x^2 + \tfrac{1}{2}K_2y^2\,. \qquad (1)$$

The electronic term of the Hamiltonian is as follows

$$H_R^{el} = W\sum_{i=1}^{4}\sum_{\sigma} a_{i\sigma}^{+}a_{i\sigma}$$
$$-\beta_1\sum_{\sigma}(a_{1\sigma}^{+}a_{2\sigma} + a_{3\sigma}^{+}a_{4\sigma} + \text{h.c.})$$
$$-\beta_2\sum_{\sigma}(a_{2\sigma}^{+}a_{3\sigma} + a_{1\sigma}^{+}a_{4\sigma} + \text{h.c.})$$
$$+\tfrac{1}{2}\gamma\sum_{i,\sigma} a_{i-\sigma}^{+}a_{i-\sigma}a_{i\sigma}^{+}a_{i\sigma}\,, \qquad (2)$$

where $a_{i\sigma}^{+}$ ($a_{i\sigma}$) are operators of creation (annihilation) of an electron having a spin projection σ ($\sigma = 1/2$ or $-1/2$; henceforth the electron spin projection will be denoted by a subscript α or β) occupying an AO $|i\rangle$; $W<0$ is a parameter characterizing the attraction of an electron to the core; $\gamma>0$ is a parameter of the Coulombic repulsion between electrons occupying the same AO; $\beta_1>0$ and $\beta_2>0$ are bond resonance parameters (electron transition parameters) of electrons between adjacent AOs, which we assume to depend linearly on the values x and y characterizing the bond deformation of the cyclobutane ring:

$$\beta_1 = \beta_1^0 + \beta' x\,, \quad \beta_2 = \beta_2^0 + \beta' y\,.$$

It was pointed out in ref. [9] that the linear approx-

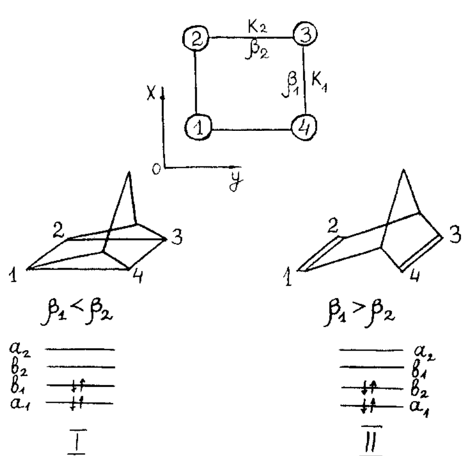
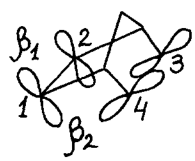


Fig. 1. Schematic arrangement of atoms, atomic and molecular orbitals in quadricyclene (I) and norbornadiene (II).

imation for β_1 (the resonance integral between two π-overlapping AOs) was valid while the variation of π-bond length is small ($|x| \lesssim 0.3$ Å). The similar approximation for β_2 is the rough simplification which we assume to be acceptable through the limited range of y variation. The parameters β_1 and β_2 correspond to different types of AO overlap:



Two parameters – β'_1 and β'_2 – are necessary to describe the dependence of β_1 and β_2 on the interatomic distance. For the sake of simplicity we assume them to be equal: $\beta'_1=\beta'_2=\beta'$. The second and the third terms in (1) describe the elastic energy of the core, on which the four electrons are located. Like in the theory of conjugated systems [9], we assume $x\leqslant 0$, $y\leqslant 0$ for the points corresponding to the minima on the ground state PES and the bond lengths are set as follows:

$$r_{12}=x+R_x^0\,,\quad R_x^0=1.54\ \text{Å}\,,$$

$$r_{23}=y+R_y^0\,,\quad R_y^0=2.6\ \text{Å}\,.$$

The elasticity constants K_1 and K_2 are twice the constants for the bonds (12), (34), and (23), (14), respectively.

The matrix of the electronic term of the Hamiltonian H_R^{el} in the basis of the four-electron Slater determinants $|a_1^2b_1^2\rangle$, $|a_1^2b_2^2\rangle$ (term symmetry A_1) and $|a_1^2b_{1\alpha}b_{2\beta}\rangle$, $|a_1^2b_{1\beta}b_{2\alpha}\rangle$ (term symmetry A_2), consists of two blocks

$$\begin{pmatrix} 4W-4\beta_1+\gamma & \gamma/4 \\ \gamma/4 & 4W-4\beta_2+\gamma \end{pmatrix}_{A_1}$$

$$\begin{pmatrix} 4W-2(\beta_1+\beta_2)+\gamma & -\gamma/4 \\ -\gamma/4 & 4W-2(\beta_1+\beta_2)+\gamma \end{pmatrix}_{A_2}. \qquad (3)$$

In the basis of functions of definite total spin, i.e. a singlet and a triplet,

$$|{}^1A_2\rangle=(|a_1^2b_{1\alpha}b_{2\beta}\rangle-|a_1^2b_{1\beta}b_{2\alpha}\rangle)/\sqrt{2}\,,$$

$$|{}^3A_2\rangle=(|a_1^2b_{1\alpha}b_{2\beta}\rangle+|a_1^2b_{1\beta}b_{2\alpha}\rangle)/\sqrt{2}\,, \qquad (4)$$

the block A_2 has a diagonal form.

The different PESs of the system considered are eigenvalues of the Hamiltonian (1) depending on x and y:

$$E({}^1A_1)=F(x,y)-R(x,y)\,,$$

$$E({}^1A'_1)=F(x,y)+R(x,y)\,,$$

$$E({}^1A_2)=F(x,y)+\gamma/4\,,$$

$$E({}^3A_2)=F(x,y)-\gamma/4\,, \qquad (5)$$

where

$$F(x,y)=4W+\gamma-2(\beta_1+\beta_2)+\tfrac{1}{2}K_1x^2+\tfrac{1}{2}K_2y^2\,,$$

$$R(x,y)=[4(\beta_1-\beta_2)^2+\tfrac{1}{16}\gamma^2]^{1/2}\,.$$

The ground state PES $E({}^1A_1)$ has two local minima corresponding to the compounds I and II, and a saddle point. All the stationary points lie on a straight line defined by the equation:

$$K_1x+K_2y=4\beta'\,.$$

The parameters β_1^0, γ and K_1 are assigned the values which are commonly used for the conjugated systems [9]. The value of β' is only slightly modified in respect to the one used in ref. [9]. The values of β_2^0 and K_2 are estimated for the calculated activation energy ΔE and the heat of reaction ΔU to approximate the experimental data for the reaction I→II.

The set parameters defined as stated above,

$$\beta_1^0=2.5\ \text{eV}\,,\quad \beta_2^0=0.02\ \text{eV}\,,$$

$$\beta'=-4.75\ \text{eV/Å}\,,\quad \gamma=6\ \text{eV}\,,$$

$$K_1=92\ \text{eV/Å}^2\,,\quad K_2=16.65\ \text{eV/Å}^2\,, \qquad (6)$$

leads to $\Delta E_{calc}=1.41$ eV and $\Delta U_{calc}=1.01$ eV compared with $\Delta E_{obs}=1.45$ eV [10] and $\Delta U_{obs}=1.03$ eV [11]. The minimum I is located in the point ($x=0$, $y=-1.14$ Å) and the minimum II is in the point ($x=-0.2$, $y=-0.036$ Å) (see fig. 2).

3. The interaction of the reacting system with a catalyst and an effective Hamiltonian of the catalytic complex

The Hamiltonian of the combined system RM has the form:

$$H=H_M+H_R+H_I+H_C\,, \qquad (7)$$

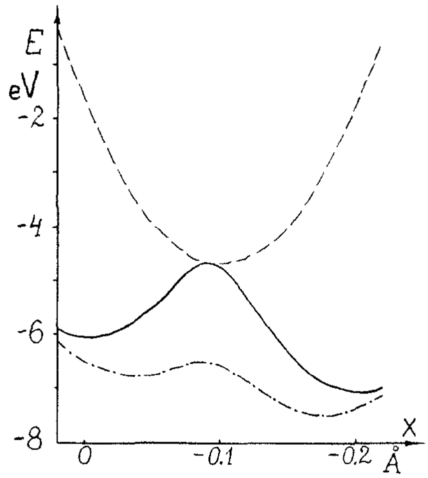


Fig. 2. Sections of the potential energy surface for the reacting system along the straight line $K_1x+K_2y=4\beta'$. Reagents without a catalyst: (——) $E(^1A_1)$; (– – –) $E(^3A_2)$; reagents with CoTPP as a catalyst: (–·–·–) $E(x)$ by eq. (23) with $g=-3$ eV.

where H_R is the Hamiltonian of reagents (1), H_M is the Hamiltonian of the catalyst. We consider the following coordination of I with metalloporphyrin: the plane of the cyclobutane ring of I is parallel to that of porphyrin, the ring's centre is located right above the metal, and the C–C bonds are normal to the metal–nitrogen bonds of the porphyrin. With this arrangement the combined system has the symmetry C_{2v}. So, the operator of resonance interaction between the reagents and a catalyst is of the form:

$$H_I=\sum_{\Gamma,m_1m_2} H_I(\Gamma,m_1,m_2)\ . \tag{8}$$

Here Γ is the orbital symmetry common to both subsystems and m_1 and m_2 label orbitals of R and M subsystems respectively. In the present case Γ may be either b_1 or b_2 and in both subsystems there exists only one orbital of either symmetry. The operator $H_I(\Gamma, m_1, m_2)$ is proportional to the resonance parameter $b^{\Gamma}_{m_1,m_2}$ for the orbitals R and M.

In our case the Hamiltonian of the resonance interaction between the reagents and the catalyst has the form

$$H_I=-b\sum_{\sigma}(M^+_{xz,\sigma}R_{b1,\sigma}+M^+_{yz,\sigma}R_{b2,\sigma}+\text{h.c.})\ ,$$

where $M^+_{xz,\sigma}$, $M^+_{yz,\sigma}$ are creation operators for an electron with the spin projection $\sigma=\pm 1/2$ on the d_{xy} and d_{yz} AOs, respectively; $R_{b_1\sigma}$, $R_{b_2\sigma}$ are the annihilation operators for an electron occupying the reagents' MO with the symmetry b_1, b_2, respectively; b is a resonance parameter which we assume to be the same for $\Gamma=b_1$ and b_2. The operator H_C of the Coulombic interaction between the catalyst and reagents is taken in the form

$$H_C=g_{MR}(\hat{N}_M-Z_M)(\hat{N}_R-Z_R)\ , \tag{9}$$

where $\hat{N}_M$ and $\hat{N}_R$ are operators of the number of electrons, and Z_M and $Z_R=4$ are the core charges in the subsystems M and R; $g_{RM}>0$ is a parameter of the Coulombic interaction between the subsystems M and R.

We estimated g_{RM} as an energy of Coulombic interaction of two point-charges located in the "centers of gravity of charges" ground state of the subsystems M and R, and found it to be ≈4.5 eV.

Now let us consider the ground state term of the Hamiltonian (7) in the basis of many-electron functions of the combined system RM. The basis RM-functions, built up of product of the R- and M-functions, possess correct symmetry, definite number of particles, and given total spin and its projection; they will be denoted as

$$|kN,k'N'\rangle =|n\ ^{2S+1}\Gamma N,n'\ ^{2S'+1}\Gamma' N';\ ^{2\bar{S}+1}\bar{\Gamma},\bar{S}_z\rangle\ , \tag{10}$$

where $k=(n\Gamma S)$ and $k'=(n'\Gamma'S')$ are multi-indices for the subsystems M and R, respectively, with the numbers of electrons being N and N'. The detailed notation on the right-hand side involves the total symmetry $\bar{\Gamma}$, total spin $\bar{S}$, and it projection $\bar{S}_z$.

In the basis of the functions (10) the Hamiltonian

$$H_0=H_M+H_R+H_C\ , \tag{11}$$

has a diagonal form with the following matrix elements

$$\langle kN,k'N'|H_0|kN,k'N'\rangle=E^0(kN,k'N')$$
$$=\langle kN|H_M|kN\rangle+\langle k'N'|H_R|k'N'\rangle$$
$$+g_{MR}(N'-Z_R)(N-Z_M)\ . \tag{12}$$

The operator H_I is non-diagonal and mixes the states $|kN,k'N'\rangle$ and $|qN\pm 1,q'N'\mp 1\rangle$, which are obtained by an electron transfer between R and M.

Since the initial (I) and the final (II) states of the system R have the same number of electrons, $N'=4$, let us describe the reaction in the subspace of functions without charge transfer between M and R. The configurations with charge transfer (CT) concerned with important resonance interactions will be taken into account following the Van Vleck method [12] (cf. also ref. [13]). The contribution of the CT configurations arises as correlation corrections by going from the total Hamiltonian H to an effective one, which acts in the subspace of functions with zero charge transfer between M and R, and whose eigenvalues coincide with those of the total Hamiltonian H.

Let A be a subspace of configurations with zero charge transfer between R and M, B is the complement subspace, P_A and P_B are the projectors onto the subspaces ($P_A + P_B = 1$). Let us denote

$$H^{ij} = P_i H P_j \quad (i, j = \mathrm{A}, \mathrm{B}) . \tag{13}$$

An effective Hamiltonian H_{eff} depending on the energy E has the form [13]:

$$H_{\text{eff}}(E) = H^{\text{AA}} + H^{\text{AB}} R^{\text{B}}(E) H^{\text{BA}} , \tag{14}$$

where

$$R^{\text{B}}(E) = (E P_{\text{B}} - H^{\text{BB}})^{-1} ,$$

is the resolvent operator for H^{BB}.

Taking into account eqs. (10)–(14) the following explicit expression can be derived for the matrix element of $H_{\text{eff}}(E)$

$$\begin{aligned}\langle kN, k'N' | H_{\text{eff}} | lN, l'N' \rangle &= \delta_{kl}\delta_{k'l'} E^0(kN, k'N') \\ &+ \sum_{qq'} \frac{\langle kN, k'N' | H_1 | qN+1, q'N'-1 \rangle}{E - E^0(qN+1, q'N'-1)} \\ &\times \langle qN+1, q'N'-1 | H_1 | lNl'N' \rangle \\ &+ \sum_{qq'} \frac{\langle kN, k'N' | H_1 | qN-1, q'N'+1 \rangle}{E - E^0(qN-1, q'N'+1)} \\ &\times \langle qN-1, q'N'+1 | H_1 | lNl'N' \rangle .\end{aligned} \tag{15}$$

This expression resembles very closely that for the second-order correction in the perturbation theory. The operator $H_{\text{eff}}(E_0^0)$, where E_0^0 is the ground state energy for the operator H_0, is exactly the Hamiltonian obtained on partial diagonalization of the operator $H = H_0 + H_1$ in the second-order perturbation theory, with H_1 as a perturbation.

Non-diagonal matrix elements of the operator $H_{\text{eff}}(E)$ obey selection rules: each intermediate state $|qN \pm 1, q'N' \mp 1\rangle$ should have the same total symmetry $\bar{\Gamma}$, total spin $\bar{S}$, and spin projection $\bar{S}_z$, as the functions $|kN, k'N'\rangle$ and $|lN, l'N'\rangle$.

4. Variational approach to the calculation of the ground state energy of the effective Hamiltonian

The potential energy surface for the complex RM is the lowest eigenvalue $E = E(x, y)$ of the operator H_{eff}, which should be found as a solution of the equation

$$\langle \psi | H_{\text{eff}}(E) | \psi \rangle = E , \tag{16}$$

where the variational function

$$\psi = \sum_{kk'} c_{kk'} |kN, k'N'\rangle , \quad \sum_{kk'} |c_{kk'}|^2 = 1 , \tag{17}$$

is a linear combination of functions belonging to the subspace A, with unknown coefficients $c_{kk'}$.

Eqs. (16) and (17) have to be solved by iterations in each point (x, y). Assuming an initial value for $E = \mathscr{E}_0$, we derive the Hamiltonian $H_{\text{eff}}(\mathscr{E}_0)$, then its lowest eigenvalue $\mathscr{E}_1$ should be found; then the procedure is iterated starting from $\mathscr{E}_1$ until convergence in $\mathscr{E}$ is achieved. The last iteration gives also the function ψ. As the first approximation let us confine ourselves to the Hamiltonian $H^*_{\text{eff}} = H_{\text{eff}}(E_0^0)$, where E_0^0 is the lowest eigenvalue of the Hamiltonian H_0 at the point (x, y). Then eq. (16) is reduced to

$$E = \langle \psi | H^*_{\text{eff}} | \psi \rangle . \tag{18}$$

The variational function is assumed to be a linear combination of two eigenfunctions of H_0, ψ_0 (being the ground state of H_0) and ψ_1, corresponding to the lowest eigenvalue of H_0, for which the matrix element $\langle \psi_0 | H^*_{\text{eff}} | \psi_1 \rangle$ is non-vanishing.

In the present case ψ has the form:

$$\psi = \psi_0 \cos\varphi + \psi_1 \sin\varphi , \tag{19}$$

with one variational parameter φ. The functions ψ_0 and ψ_1 are defined as

$$\begin{aligned}\psi_0 &= |{}^{2S+1}\Gamma N, {}^1\mathrm{A}_1 4; {}^{2\bar{S}+1}\bar{\Gamma} N+4\rangle , \\ \psi_1 &= |{}^{2S'+1}\Gamma' N; {}^3\mathrm{A}_2 4; {}^{2\bar{S}+1}\bar{\Gamma} N+4\rangle ,\end{aligned} \tag{20}$$

where $\bar{\Gamma} = \Gamma$, $\bar{S} = S$. The spatial symmetry Γ' and spin S' are determined by the condition that the functions ψ_0 and ψ_1 should have the same spatial symmetry $\bar{\Gamma}$

and spin $\bar{S}$. Taking into account the explicit form of ψ_0 we conclude that $\bar{\Gamma}$ should be equal to Γ, and $\bar{S}$ should be equal to S due to the relation ${}^{2S+1}\Gamma \otimes {}^1A_1 = {}^{2S+1}\Gamma$. So Γ' should be such that its direct product with A_2 gives Γ and S' should be equal to $S \pm 1$. In eq. (20) we use the detailed notation of eq. (10) (with $\bar{S}_z$ omitted) for the functions ψ_0 and ψ_1. Their averages with H_0 (E_0^0 and E_1^0) are defined by the following expressions:

$$E_0^0 = \langle \psi_0 | H_0 | \psi_0 \rangle = \langle {}^{2S+1}\Gamma N | H_M | {}^{2S+1}\Gamma N \rangle + E({}^1A_1) , \quad (21)$$

$$E_1^0 = \langle \psi_1 | H_0 | \psi_1 \rangle = \langle {}^{2S'+1}\Gamma' N | H_M | {}^{2S'+1}\Gamma' N \rangle + E({}^3A_2) . \quad (22)$$

The PES to be found is now determined by minimizing the expression

$$E(\varphi) = a \cos^2\varphi + d \sin^2\varphi + g \sin 2\varphi . \quad (23)$$

The minimum takes place at $\varphi = \varphi_0$, where

$$\mathrm{tg}\, 2\varphi_0 = \frac{2g}{a-d} , \quad (24)$$

and

$$a = \langle \psi_0 | H_{\mathrm{eff}}^* | \psi_0 \rangle , \quad d = \langle \psi_1 | H_{\mathrm{eff}}^* | \psi_1 \rangle , \quad g = \langle \psi_0 | H_{\mathrm{eff}}^* | \psi_1 \rangle . \quad (25)$$

Taking into account eqs. (15), (23)–(25) the ground state PES can be expressed as

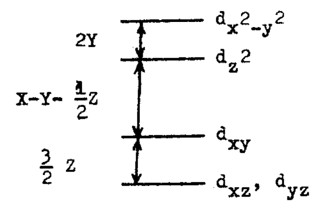
$$E(x, y) = E({}^1A_1) \cos^2\varphi_0 + E({}^3A_2) \sin^2\varphi_0 + B(x, y) , \quad (26)$$

where the first two terms represent an admixture of the excited R state to the ground one, and the last term combines the remaining contributions from (23). The minimum of the excited term is located near the maximum of the ground term, in the region of the reaction barrier (see fig. 2 and eqs. (5)). Hence, if we take into account only the first two terms in eq. (26), we see that the barrier height for the reaction I→II decreases while φ_0 is non-zero.

5. Comparative estimates of the catalytic activity of the complexes CoTPP and MnTPP

Let us now compare the values of the parameter characterizing the catalytic activity, tg $2\varphi_0$, for cobalt tetraphenylporphyrin (CoTPP) and manganese tetraphenylporphyrin (MnTPP), of which the first displays catalytic activity in the reaction I→II, whereas the second is an analogue of the catalytically inactive d^5 complexes Fe(III)TPP$^+$ and MnPc.

Now consider the crystal field model for the Hamiltonian H_M in the d approximation, i.e. when all properties of the ions Mn^{2+} ($3d^5$) and Co^{2+} ($3d^7$) are determined by merely their d electrons. The matrix representations for H_M in this approximation were built up in ref. [14], taking into account the Coulombic interactions in the d^N shell, for the C_{4v} symmetry. The splitting of levels in the ligand field is described by three parameters, X, Y, Z. Their meaning is evident from the scheme of the energy levels of d electrons:



The Coulomb interaction of d electrons is assumed to be the same as in the free ion and determined by the Racah parameters A, B, C. In the case of CoTPP the splitting parameters evaluated from the ESR spectra are [15]:

Co: $X = 1.3$ eV, $Y = 2$ eV, $Z = -0.5$ eV .

For MnTPP the splitting parameters are taken to be 1.3 times as less as those for CoTPP

Mn: $X = 1$ eV, $Y = 1.54$ eV, $Z = -0.38$ eV .

The latter parameter set takes into account that in the octahedral complexes the parameter 10 Dq (which is similar to X) for Mn(II) complexes is, on the average, just 1.3 times smaller than for the Co(II) complexes [16].

According to ref. [15], the ground state of CoTPP has the symmetry ${}^2A_1$, and, hence, the symmetry of ψ_0 is ${}^2A_1 \otimes {}^1A_1 = {}^2A_1$. The lowest energy state of CoTPP, which would allow the state ψ_1 to have the same symmetry, is the state ${}^4B_2$. (In the system RM, which has the symmetry C_{2v}, the state ${}^4B_2$ reduces to ${}^4A_2$, and then ${}^4A_2 \otimes {}^3A_2 = {}^2A_1 \oplus {}^4A_1 \oplus {}^6A_1$.)

In the case of CoTPP the expansion (17) could involve the function $\psi_2 = |{}^4A_2 7, {}^3A_2 4\rangle$. According to ref. [15], the energy corresponding to this function

$E_2^0 = \langle \psi_2 | H_0 | \psi_2 \rangle$

is slightly higher than that for $\psi_1 = |{}^4B_2 7, {}^3A_2 4\rangle$. Hence, we may neglect ψ_2 in one rough estimation based on the expansion (19).

Let us consider the effect of the configuration interaction in the catalyst on its catalytic activity.

Within the self-consistent field (SCF) approximation (configuration interaction is absent) the electronic structure of the ground state of CoTPP of symmetry ${}^2A_1$ is characterized by a single configuration of d electrons $\{e^4 b_2^2 a_1\}\ {}^2A_1$ [6,15]. According to eq. (15) the function ψ_0 corresponding to such a configuration of d electrons of the metal atom would not give non-vanishing matrix elements of $H^*_{\rm eff}$ with the function ψ_1, which has the configuration $\{e^2({}^3A_2) b_2^2 a_1^2 b_1\}\ {}^4B_2$. However, due to the configuration interaction the ground state of CoTPP of symmetry ${}^2A_1$ has an admixture of the d electron configuration $\{e^2({}^1B_1) b_2^2 a_1^2 b_1\}\ {}^2A_1$:

$$\psi_0(\mathrm{Co}) = u_0 |\{e^4 b_2^2 a_1\}{}^2A_1\rangle + \dots$$
$$+ u |\{e^2({}^1B_1) b_2^2 a_1^2 b_1\}{}^2A_1\rangle .$$

The configuration interaction matrix was calculated using the expressions for the matrix elements given in ref. [14] with the parameter values of X, Y, Z and Racah parameters as given in ref. [15]. Diagonalizing the matrix we estimated u to be ≈ 0.1. As a result, there is a non-zero matrix element of $H^*_{\rm eff}$ with the functions ψ_0 and ψ_1, proportional to u.

According to ref. [17], the ground state of MnTPP is the single configuration having the symmetry ${}^6A_1$, which is also the symmetry of ψ_0 and ψ_1. The first excited term of MnTPP which affords $\psi_1({}^6A_1)$ is the ${}^4A_2$ term.

There is another function, $\psi_2 = |{}^4B_2 5, {}^3A_2 4\rangle$, that could be taken into account, but as the energy of this state is higher than that of ψ_1 we may neglect it like in the case of CoTPP.

Let us now estimate the value of $\mathrm{tg}\, 2\varphi_0$ using eq. (23). If we assume the corrections to the diagonal elements of H_0 (i.e. the sums over qq' in eq. (15)) in the formulae for a and d to be roughly equal and, hence, being cancelled in the difference $(a-d)$, we arrive at the following estimate:

$$a-d = E_{\rm M}^0({}^{2S+1}\Gamma) - E_{\rm M}^0({}^{2S'+1}\Gamma') + E({}^1A_1)$$
$$- E({}^3A_1) \equiv -\Delta E_{\rm M}^0 - \Delta E_{\rm R}^0 . \qquad (27)$$

The observed data for CoTPP give [15]

$$\Delta E_{\rm Co}^0 = E_{\rm Co}^0({}^4B_2) - E_{\rm Co}^0({}^2A_1) = 0.21\ \mathrm{eV} .$$

The term energies $E_{\rm Mn}^0$ for MnTPP were calculated as follows. The matrix of the Hamiltonian $H_{\rm M}$ was calculated using the expressions for the matrix elements cited in ref. [14] with the parameter values of X, Y, and Z estimated above and Racah parameters $B=0.1$ eV, $C=0.5$ eV from ref. [16]. Transforming the corresponding matrices to a diagonal form we found the energies of the terms ${}^4A_1$ and ${}^6A_2$.

There are three states of the ion Mn^{2+} of symmetry ${}^4A_2$ constructed from the three electronic configurations [14]:

$$|{}^4A_2, i\rangle = \sum_{k=1}^{3} A_{ik} |\varphi_k\rangle ,$$

$$|\varphi_1\rangle = |e^2({}^3A_2) b_2^2 a_1 ({}^2A_1)\rangle ,$$
$$|\varphi_2\rangle = |e^2({}^3A_2) a_1 b_1^2 ({}^2A_1)\rangle ,$$
$$|\varphi_3\rangle = |e^2({}^1A_1) b_2 a_1 b_1 ({}^4A_2)\rangle .$$

Taking into account the electronic configuration of the ground state of d electrons, $|{}^6A_1\rangle = |e^2({}^3A_2) b_2 a_1 b_1 ({}^4A_2)\rangle$ [14], and recalling that, according to eq. (15),

$$\langle \psi_0 | H^*_{\rm eff} | \varphi_k 5, {}^3A_2 4\rangle = 0 \quad \text{for } k=1,2 ,$$

the non-diagonal matrix element $\langle \psi_0 | H^*_{\rm eff} | \psi_1 \rangle$ assumes the form

$$\langle \psi_0 | H^*_{\rm eff} | \psi_1 \rangle$$
$$= \sum_{k=1}^{3} \langle \psi_0 | H^*_{\rm eff} | \varphi_k 5, {}^3A_2 4\rangle A_{ik}$$
$$= A_{i3} \langle \psi_0 | H^*_{\rm eff} | \varphi_3 5, {}^3A_2 4\rangle .$$

We found that the state $|{}^4A_2, 1\rangle$ with the lowest excitation energy (≈ 1.7 eV) involves mainly the configuration φ_1 ($A_{11}=0.99$, $A_{13} \ll 1$); the corresponding non-diagonal matrix element with ψ_0 is

$$\langle \psi_0 | H^*_{\rm eff} | \psi_1 \rangle \approx A_{13} \approx 0 .$$

The state $|{}^4A_2, 2\rangle$ with the excitation energy of ≈ 5 eV contains a noticeable contribution of the configuration φ_3 ($A_{23} \approx 0.9$); precisely this state should be employed in the construction of ψ_1 by the formula (19). The estimates of the excitation energies for the d shell are consistent with the observed data for Mn(II)TPP [18]: according to these data the energies of the π–π* transitions are less than the energy of the first d–d transition, which amount to 2 eV. Hence, the required energy difference for MnTPP is estimated to be

$$\Delta E^0_{\mathrm{Mn}} = E^0_{\mathrm{Mn}}(^4\mathrm{A}_2, 2) - E^0_{\mathrm{Mn}}(^6\mathrm{A}_1) = 5.2\ \mathrm{eV}\,.$$

In order to estimate g by the formulae (15), (20), (25) let us count, first of all, the number of non-zero terms in the sums over qq'. This number is equal to that of the intermediate states (qq') of required symmetry and spin in the d^8 and d^6 shells of CoTPP, or in the d^4 and d^6 shells for MnTPP. Taking into account the addition rules for spins and the explicit expression for H_I, the symmetry of these states is found to be $^3\mathrm{B}_i$ ($i=1, 2$) for CoTPP, and $^5\mathrm{B}_i$ for MnTPP (C_{2v} symmetry). The number of states of symmetry $^{2S+1}\mathrm{B}_i$ is twice the number of states $^{2S+1}\mathrm{E}$ (C_{4v} symmetry), and, according to ref. [14], the respective numbers are $N_{\mathrm{Co}}=15$, $N_{\mathrm{Mn}}=2$. The number of non-zero terms in the expressions for g is, by eq. (15), $\tilde{N}_{\mathrm{Co}}=30$ for CoTPP and $\tilde{N}_{\mathrm{Mn}}=4$ for MnTPP. Neglecting a weak dependence of the parameter g on the coordinates (x, y), its value can be estimated by the theorem of the mean value:

$$g = \sum_{\nu \in \mathrm{B}} \frac{\langle kNk'N' | H_\mathrm{I} | \nu \rangle \langle \nu | H_\mathrm{I} | lNl'N' \rangle}{E - E_\nu} \approx -\tilde{N}_{\mathrm{Co}} \frac{ub^2}{\Delta E_g}\,,$$

where the summation is performed over the states with the charge transfer between the metal and reagents. Let us assume the average energy of the states with the charge transfer to be $\Delta E_g \approx 15$ eV, and the average value of the resonance parameter to be $b \approx 4$ eV. The latter estimate follows from the parametrization for the resonance integrals [18] for the transition metals. The distance between the Co and C atoms is estimated as $R_{\mathrm{CoC}} = R_{\mathrm{Co}} + R_{\mathrm{C}} - 0.09\,|\chi_{\mathrm{Co}} - \chi_{\mathrm{C}}| = 1.87$ Å, where R_{Co} and R_{C} are the respective covalent radii, χ_{Co} and χ_{C} are Pauling's electronegativities, and the exponential parameters for the Slater AOs for the Co atom are taken according to ref. [6]. Then, for $\tilde{N}_{\mathrm{Co}}=30$ we obtain $g \approx -3$ eV. Finally, the potential curve along the reaction path can be found by eqs. (23) and (24) with the parameter g just estimated, and the value of the activation energy, $\Delta E_{\mathrm{theor}}$(CoTPP), is estimated to be 0.22 eV (fig. 2).

Within the suggested approach one can explain a decrease in the catalytic activity of complexes, arising on addition of small amounts of compounds capable of being axially coordinated to the Co atom in the metalloporphyrin (as, e.g., pyridine [2]). Apart from an evident explanation that the coordination of an inert ligand hinders the coordination of the reagent [2], the coordination of pyridine reduces the own catalytic activity of CoTPP. According to the data [15], the energy of the excited states $^4\mathrm{B}_2$ and $^4\mathrm{A}_2$ in the complexes Py–CoTPP is essentially higher in comparison with the corresponding energies of the free Co-porphyrin. Eqs. (24) and (27) show that this leads to the growth of the activation energy for the reaction with Py–CoTPP as catalyst in comparison with CoTPP.

Let us now compare the values of $\mathrm{tg}\,2\varphi_0$ for the complexes CoTPP and MnTPP. Since in the case of MnTPP the difference $a-d$, i.e. the denominator of $\mathrm{tg}\,2\varphi_0$, is 10 times as great as for CoTPP, while the number of terms in the numerator is 7 times less, we arrive at the following estimate

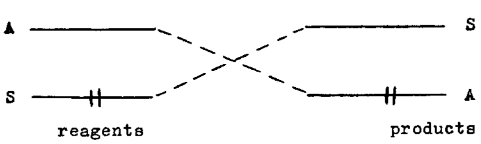
$$\frac{(\mathrm{tg}\,2\varphi_0)_{\mathrm{MnTPP}}}{(\mathrm{tg}\,2\varphi_0)_{\mathrm{CoTPP}}} = 10^{-1}\text{–}10^{-2} \qquad (28)$$

near the reaction barrier. The value of this ratio shows that the catalytic activity of MnTPP should be essentially less than the activity of CoTPP. The ground state of Fe(III)TPP has the total spin $S=5/2$, like the ground state of MnTPP, and the value of the parameter $\mathrm{tg}\,2\varphi_0$ for Fe(III)TPP estimated under the same assumptions as for MnTPP leads to a close result. This is consistent with the catalytic inactivity of the complex Fe(III)TPP observed in ref. [2] in the reaction considered. In the case of the other inactive d^5 complex MnPc [2] no direct information is available on the spin of the ground state of the catalyst under the reaction conditions. In the crystalline MnPc the term $^4\mathrm{A}_2$ is the ground state [19]. The excited state $^6\mathrm{A}_1$ has the energy ≈ 0.075 eV, and in solution this state may become the ground one. This conclusion is based on the fact that the existence of MnPc in the state $^4\mathrm{A}_2$ in the crystal is governed by an additional splitting of the d-electron levels of the Mn atom arising due to the nitrogen atoms of the adjacent molecules of MnPc [19]. The additional splitting vanishes in solution.

Besides, the low-lying state $^4A_2$ in MnPc refers, like in MnTPP, to the configuration $\{e^2(^3A_2)b_2^2a_1\}$ [19]. As it was already pointed out, this state, even being close in energy to the ground state $^6A_1$, does not contribute to the catalytic activity. For the other state, $^4A_2$, with the configuration $\{e^2(^1A_1)b_2a_1b_1\}$, which could contribute to the catalysis, the energy difference ΔE^0_{Mn} is ≈ 3 eV. This value indicates, according to eq. (24), that MnPc should not display any catalytic activity.

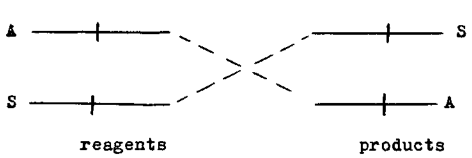
6. Discussion

It is of interest to discuss a series of results obtained in this work from the viewpoint of the known theoretical backgrounds [5]. According to the Woodward–Hoffman rules [8] the reaction is expected to have a considerable activation energy if in the course of the reaction there takes place a reoccupation of the (doubly occupied) orbitals of different symmetry,



(A)

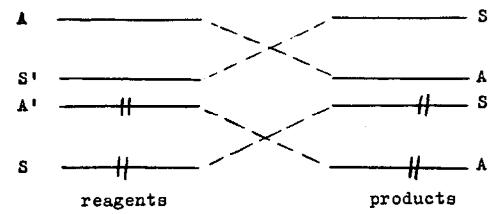
Such a situation is usually referred to as a "symmetry forbidden" reaction. It is well known that if a reaction is symmetry forbidden in the ground state, then it is symmetry allowed in the excited state. This may be illustrated by the following scheme:



(B)

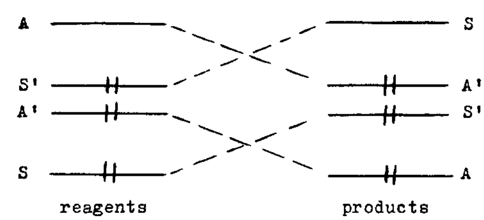
So the reaction becomes allowed when intersecting orbital levels are both singly occupied.

The MS theory of catalysis takes into account the orbitals of the catalyst (A′S′) which have the same symmetry as the orbitals of the reagent (A, S).



(C)

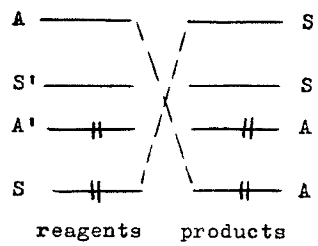
In this case, when the catalyst's orbital A′ is doubly occupied, no reoccupation of the orbitals of different symmetry takes place, and the reaction is allowed. However, as it was pointed out [2], the orbitals S′, A′ in the case of CoTPP are the d_{xz}, d_{yz} orbitals of the Co atom. In the ground state of CoTPP, calculated in the SCF approximation, both these orbitals are doubly occupied [6], and this leads to the following diagram of the energy levels:



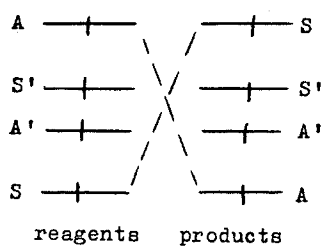
(D)

In this case the reaction requires a reoccupation of orbitals of different symmetry, so the reaction should be forbidden. The failure of the MS theory [5] to explain the catalytic activity of CoTPP (and similar complexes) in the isomerization of quadricyclane to nonbornadiene is connected with the above considerations.

In the course of our investigation we found that the effect of the catalyst is not limited to supplying the orbitals of the appropriate symmetry. Of more importance is the catalyst-induced partitional population of an excited state of the reagent subsystem which may undergo the symmetry allowed reaction transition. That means that the superposition of the following correlation diagrams E_1 and E_2,



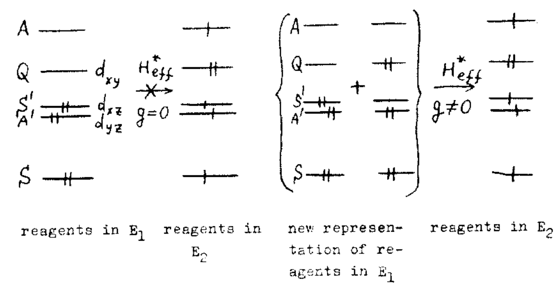
E_1



E_2

takes place. These diagrams are entirely different from the ones used in the MS theory. The diagram E_1 represents the symmetry forbidden reaction (like diagram A) and E_2 the symmetry allowed one (like B). The partial contributions of the diagrams E_1 and E_2 depend on the value of tg $2\varphi_0$, i.e. on the ratio of the effective interaction parameter (g) to the excitation energy ($a-d$) of the reagent state represented by the diagram E_1 into the state corresponding to the diagram E_2. Note that due to the nature of the operator $H^*_{\rm eff}$, the configuration interaction takes place only for the configurations which differ by states of two electrons (one in the catalyst subsystem and the other in the reagents).

In the ground state of the complex of CoTPP with quadricyclane the orbitals A′ and S′ (d_{xy} and d_{yz} of Co respectively) are both doubly occupied. So, while being confined to a one-configuration approximation, e.g., the SCF method, no excitation of the ground state of the reagents can produce a configuration with four unpaired electrons which corresponds to diagram E_2. That is the reason for the matrix elements of $H^*_{\rm eff}$ for E_1 to E_2 transition to vanish, making the contribution of E_2 to be zero. However, a configuration A'^2Q^2, where Q is some d orbital other than S′, contributes to the ground state of CoTPP. This contribution was found by considering the Coulomb interactions of all d electrons of the complex. The following diagrams illustrate the insufficiency of the SCF approximation for describing the ground state of reagent in the case of a d^7 complex of Co(II) and the necessity for inclusion of all d-electron configurations into the ground state of catalyst:



In our calculation the ground state $^2A_1$ of the complex CoTPP was a superposition of the five configurations of d electrons [14]. Of these configurations the one $\{e^4b_2^2a_1\}$ plays the role of the configuration $A'^2S'^2$ (the active e orbitals are fully occupied), while the configuration $\{e^2(^1B_1)b_2^2a_1^2b_1\}$ takes the part of the $A'^2Q'^2$ configuration. As it was pointed out, it is the admixture of this configuration that gives rise to a non-zero non-diagonal matrix element $\langle\psi_0|H^*_{\rm eff}|\psi_1\rangle$ for CoTPP. The interpretation based on our calculations account for the catalytic activity of CoTPP without evoking the p orbitals of ligands in contrast to ref. [2].

The consideration of the configuration interaction is of vital importance for studying catalytic processes. The language of correlation diagrams is natural for the SCF approximation and that is why it looks so unwieldy when applied to the theory of catalysis.

The resume of the present study is as follows: the represented theory relates the catalytic activity to the physical properties of catalyst. These properties are strongly dependent on the number of d electrons in the transition metal complex. Sometimes it can account for the great different catalytic activities of complexes of different metals(e.g., Co(II) and Mn(II) in the case at hand).

Minor differences in catalytic activity of complexes involving the same number of d electrons are caused by the differences in energy of the excited states. Lower catalytic activity of plane complexes of Co(II) with Schiff bases (Co(Salen)) compared to CoTPP, was observed in ref. [2]. From our point of view this is directly connected to the differences in g-

factor values of these complexes: $g_{\parallel}=1.798$ for CoTPP [15] and $g_{\parallel}=1.833$ for Co(Salen) [20]. For a plane-square complex in accord with ref. [15] $g_{\parallel}$ has the negative term $-8\eta_{11}^2$, where η_{11}^2 is the weight of a $^4B_2$-function in the ground state ψ_g of the complex:

$$\psi_g=\eta_0\,|^2A_1\rangle+...+\eta_{11}\,|^4B_2\rangle+....$$

The contribution of $|^4B_2\rangle$ to the ground state η_{11} is proportional to $\zeta/\Delta E^0_{Co}$, where $\Delta E^0_{Co}=E^0(^4B_2)-E^0(^2A_1)$ and ζ is a spin–orbit constant. Both the increase in the catalytic activity (reflected by $\mathrm{tg}\,2\varphi_0$) and the decrease in $g_{\parallel}$ are governed by the decrease in ΔE^0_{Co}. This explains the existence of the above-mentioned correlation.

Finally, the purely formalistic treatment of the simple model of the reaction, which involves so many assumptions, estimates and simplifications, allowed us to rationalize the complete set of the difficulties and concepts connected to the problem of catalytic activity.

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