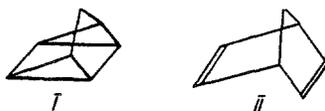


A method is proposed for calculation of the catalytic activity of the complexes of transition metals. An effective Hamiltonian describing the behavior of the reagents in the presence of the catalyst is formulated, and a catalytic activity index  $\tan^2 \varphi_0$  is introduced. The isomerization of quadricyclane to norbornadiene is considered. It is shown that the index in the case of the catalytically active low-spin complex CoTPP is two orders of magnitude larger than in the case of the catalytically inactive high-spin complex MnTPP and the analogous Fe(III)TPP and MnPc complexes.

Investigation of the nature of the catalytic activity of metal complexes in various reactions is an important task in organic synthesis and homogeneous catalysis. As an example we will consider the isomerization of quadricyclane (I) to norbornadiene (II) [1-4]:



This symmetry-forbidden  $2\pi + 2\pi$  reaction has many analogs and has evidently been studied experimentally better than the others. The catalysis of this reaction by various transition metal complexes was studied in [2] and interpreted in terms of the Mango-Schachtschneider (MS) theory [5].

As noted in [2], explanation of the catalytic activity of the various complexes in terms of the MS theory comes up against serious difficulties. The combined system RM, consisting of the reacting molecule R coordinated with the catalyst M, conserves orbital symmetry in the transition from the initial to the final state on account of the redistribution of the electrons among the orbitals of M and R; the establishment of this fact is the object of the MS theory. In the case of the catalysis of the isomerization of quadricyclane to norbornadiene difficulties appear in the explanation of the catalytic activity of the complexes CoTPP (Cotetraphenylporphyrin) and MnPc (Mn-phthalocyanine). As shown in [2], in CoTPP (total spin  $S = 1/2$ ) and in other low-spin complexes of Co(II) the d orbitals with  $b_1$  and  $b_2$  symmetry ( $d_{xz}$ ,  $d_{yz}$ ) are fully occupied [6] and cannot accept electrons from the corresponding MOs of the R system. In MnPc, on the other hand, each of the orbitals  $d_{xz}$  and  $d_{yz}$  is only occupied by one electron [6] and could participate in the repopulation of the orbitals of the reagent. In the latter case the requirements of the MS theory are fulfilled, and the complexes of Mn(II) and also the isoelectronic high-spin complexes of Fe(III) must be catalytically active, and this contradicts experiment [2]. During explanation of the reaction in terms of vibronic theory [7] the same difficulties evidently arise as with the MS theory. In vibronic theory, as in the MS theory, a major role in the activation of the molecule is played by the redistribution of electrons between the occupied and unoccupied MOs of the activated molecule on account of its interaction with the catalyst. As already stated, there are greater possibilities for such redistribution in the case of the complexes of Mn(II) and Fe(III) than in the case of the complexes of Co(II), but only the Co(II) complexes and not the Mn(II) and Fe(III) complexes are catalytically active.

The difficulties encountered in the application of the theory [5, 7] are explained by the disregard of the electronic correlation effects both in the subsystems R and M and in the combined system RM. As will be shown below, a major role in the theory is played by the

L. Ya. Karpov Scientific-Research Physicochemical Institute, Moscow. Translated from *Teoreticheskaya i Éksperimental'naya Khimiya*, Vol. 24, No. 4, pp. 398-406, July-August, 1988. Original article submitted December 10, 1985; revision submitted January 21, 1987.

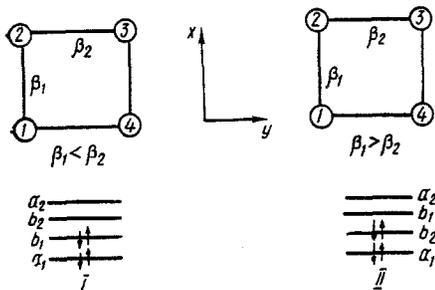


Fig. 1

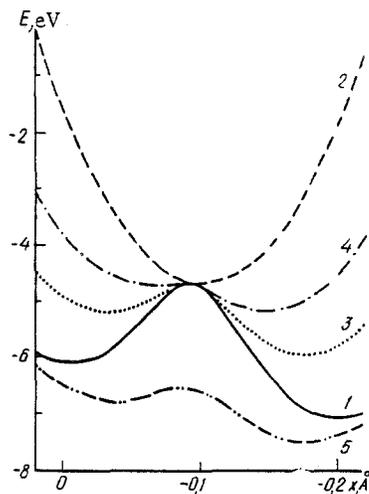


Fig. 2

Fig. 1. Diagram of the mutual arrangement of the atomic orbitals and energy levels of the molecular orbitals with various symmetries for quadricyclane (I) and norbornadiene (II) with various values for the resonance integrals.

Fig. 2. Sections of the potential energy ( $E$ ) surfaces of the reacting system along the  $K_1x + K_2y = 4\beta'$  line, on which the extremal points lie, as a projection onto the plane ( $E, x$ ): 1)  $E(^1A_1)$ ; 2)  $E(^3A_2)$ ; 3)  $3/4 E(^1A_1) + 1/4 E(^3A_2)$ ; 4)  $1/2 E(^1A_1) + 1/2 E(^3A_2)$ ; 5)  $E(x)$  according to Eqs. (22) and (23) for  $g = -3$  eV.

configurations of the combined system, which are built up from the ground states of each of the subsystems  $|R_0M_0\rangle$ , from the ionized states of the subsystems  $|R^+M^- \rangle$  and  $|R^-M^+ \rangle$  (the configurations with electron transfer between R and M), and from the excited states of the subsystems  $|R^*M^* \rangle$ , where the spin of the  $R^*$  and  $M^*$  states differs from the spin of the ground states  $R_0$  and  $M_0$ . Inclusion of the configuration interaction is an essential element of the theory both during description of the catalytic processes and during interpretation of the characteristics of transition metal complexes [8]. Use of the configurations in the form of the products of the states of the subsystems R and M will make it possible (as in the "atoms in molecules" or "molecules in molecules" methods) to achieve maximum utilization of all the available information on the states of the catalyst and the reagents.

#### Model Potential Energy Surfaces for the Isomerization of Quadricyclane to Norbornadiene

The principal concept of our proposed approach involves investigation of the changes in the potential energy surface (PES) of the gas-phase reaction ( $I \rightarrow II$ ) due to the presence of the transition metal complex. Let us examine a simple model of the reaction; the electronic structure of the reacting system is determined by four electrons [the  $4\pi$  electrons of (II) or the four electrons of the cyclobutane ring in (I) in the four atomic orbitals (AO) of the four carbon atoms] in the presence of the elastic core. The remaining electrons and atoms are taken into account through the elastic constants of the core. We obtain the four adiabatic states of the system, the energies of which (PES) will only depend on two parameters, i.e., on the change in the length ( $x$ ) and width ( $y$ ) of the cyclobutane ring, which according to our proposal preserves the rectangular form during the reaction (Fig. 1). In the LCAO-MO approximation the form of the MO is determined by the symmetry of the system ( $C_{2v}$ ):

$$\begin{aligned}
 |a_1\rangle &= (|1\rangle + |2\rangle + |3\rangle + |4\rangle)/2, & |a_2\rangle &= (|1\rangle - |2\rangle + |3\rangle - |4\rangle)/2, \\
 |b_1\rangle &= (|1\rangle - |2\rangle - |3\rangle + |4\rangle)/2, & |b_2\rangle &= (|1\rangle + |2\rangle - |3\rangle - |4\rangle)/2,
 \end{aligned}$$

where the MOs with  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  symmetry are expressed in terms of the AOs of atoms 1, 2, 3, and 4. Diagrams of the  $\epsilon(\text{MO})$  energy levels for the states of systems (I) and (II) are shown in Fig. 1. In the initial state of (I)  $\epsilon(b_1) < \epsilon(b_2)$ , and in the final state (II)  $\epsilon(b_1) > \epsilon(b_2)$ , this is determined by the mutual arrangement of the atoms 1, 2, 3, and 4 and by the magnitude of the resonance parameters. The intersection (repopulation) of the MO

levels of various symmetry in the course of the reaction I → II is a characteristic feature of a reaction prohibited by orbital symmetry (the Woodward-Hoffmann rule) [9].

The Hamiltonian of the reagents is taken in the following form:

$$H_R = H_R^{el} + K_1 x^2/2 + K_2 y^2/2. \quad (1)$$

The electronic part of the Hamiltonian  $H_R^{el}$  contains the parameter of the attraction of the electron to the core  $W < 0$ , the parameter of coulombic repulsion of the electrons in one AO  $\gamma > 0$ , and the resonance parameters of the jump of electrons between neighboring AOs, which depend linearly on the changes in the distances between the atoms  $x$  and  $y$ :

$$\beta_1 = \beta_1^0 + \beta'x, \quad \beta_2 = \beta_2^0 + \beta'y \quad (\beta_{1,2}^0 > 0, \beta' < 0). \quad (2)$$

The second and third terms in Eq. (1) describe the elastic energy of the core, in which there are four electrons. As in the theory of conjugated systems [10], we will consider that the changes in the bond lengths are negative ( $x \leq 0, y \leq 0$ ) and are measured from some hypothetical lengths:  $R_x^0 = 1.54 \text{ \AA}$  and  $R_y^0 = 2.6 \text{ \AA}$ . The elasticity constants  $K_1 > 0$  and  $K_2 > 0$  are equal to twice the elasticity constants of the 1-2, 3-4, 2-3, and 1-4 bonds, respectively.

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

$$\begin{pmatrix} 4W - 4\beta_1 + \gamma & \gamma/4 \\ \gamma/4 & 4W - 4\beta_2 + \gamma \end{pmatrix}_{A_1}, \quad (3)$$

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

The block  $A_2$  is diagonalized in the transition to functions of specific total spin (singlet and triplet):

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

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

After diagonalization of (3) we obtain the PES of the investigated reaction as the energies of the states of the Hamiltonian (1), which depend on  $x$  and  $y$ :

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

$$E({}^1A_2) = F(x, y) + \gamma/4, \quad E({}^3A_2) = F(x, y) - \gamma/4, \quad (5)$$

where

$$F(x, y) = 4W + \gamma - 2(\beta_1 + \beta_2) + K_1 x^2/2 + K_2 y^2/2,$$

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

On the potential energy surface  $E({}^1A_1)$  the two minima [corresponding to (I) and (II)] and the top of the barrier (the saddle point) on the I → II path lie on the line  $K_1 x + K_2 y = 4\beta'$ . A qualitatively correct description of the reaction I → II is obtained with the following values for the parameters:

$$\beta_1^0 = 2.5 \text{ eV}, \quad \beta_2^0 = 0.02 \text{ eV}, \quad \beta' = -4.75 \text{ eV/\AA},$$

$$\gamma = 6 \text{ eV}, \quad K_1 = 92 \text{ eV/\AA}^2, \quad K_2 = 16.65 \text{ eV/\AA}^2. \quad (6)$$

The parameters of Eq. (6) are chosen so as to describe satisfactorily the energy characteristics of the reaction I → II; the calculated activation energy  $\Delta E = 1.41 \text{ eV}$  and the energy effect of the reaction  $\Delta U = 1.01 \text{ eV}$  agree well with the experimental data  $\Delta E_{\text{expt}} = 1.45 \text{ eV}$  and  $\Delta U_{\text{expt}} = 1.03 \text{ eV}$  [11, 12]. The minimum of (I) lies at the point ( $x = 0, y = -1.14 \text{ \AA}$ ), while the minimum of (II) lies at the point ( $x = 0.2 \text{ \AA}, y = -0.036 \text{ \AA}$ ) (Fig. 2).

Interaction of the Reacting System with the Catalyst and the Effective Hamiltonian of the Reagents

We represent the Hamiltonian of the combined system R + M in the form

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

where  $H_R$  is the Hamiltonian of the reagents (I) and  $H_M$  is Hamiltonian of the catalyst or the metal ion from the metal complex. We considered the following coordination of (I) on porphyrin: The plane of the cyclobutane ring of (I) is parallel to the plane of the porphyrin, the center of the ring is above the metal atom, and the C-C bonds are perpendicular to the metal-nitrogen bonds of the porphyrin. Here the combined system belongs to the  $C_{2v}$  symmetry group. The operator of the resonance interaction between the reagents and the catalyst then has the following form:

$$H_I = \sum_{\Gamma mm'} H_I(\Gamma mm'), \quad (8)$$

where in our case  $\Gamma = b_1, b_2$  and  $m = m' = 1$ . The operator  $H_I(\Gamma mm')$  is proportional to the resonance parameter  $b_{mm'}^\Gamma$  of the orbitals of R and M. The operator of the coulombic interaction between the catalyst and the reagents  $H_C$  is given by

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

where  $\hat{N}_M$  and  $\hat{N}_R$  are the operators of the number of particles;  $Z_M$  and  $Z_R = 4$  are the charges of the cores in the subsystems M and R;  $g_{MR} > 0$  is the parameter of the coulombic interaction of the subsystems M and R. Estimates of  $g_{MR}$  as the energies of coulombic interaction between the two point charges located at the "centers of gravity of the charges" in systems M and R led to a value of  $\sim 4.5$  eV.

To study the PES of the reaction with the catalyst we will consider the lowest term of the Hamiltonian (7) on the basis of the many-electron functions of the combined system RM. These basis RM functions, constructed from the products of the R and M functions, have the correct symmetry, determined by the number of particles, by the given total spin, and by its projection, and are denoted in the following way:

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

where  $k = (n\Gamma S)$  and  $k' = (n'\Gamma'S')$ , respectively, are the multi-indices of the subsystems M and R with numbers of electrons N and N'. The total symmetry  $\bar{\Gamma}$ , the total spin  $\bar{S}$ , and its projection  $\bar{S}_z$  are given from the right in expanded notation. In the basis set of the functions (10) the operator

$$H_0 = H_M + H_R + H_C \quad (11)$$

is diagonal, and its matrix elements have the following form:

$$\begin{aligned} \langle kN, k'N' | H_0 | kN, k'N' \rangle &= E^0(kN, k'N') = \\ &= \langle kN | H_M | kN \rangle + \langle k'N' | H_R(x, y) | k'N' \rangle + g_{MR}(N' - Z_R)(N - Z_M). \end{aligned} \quad (12)$$

The operator  $H_I$  is nondiagonal and mixes the states  $|kN, k'N'\rangle$  and  $|\ell N \pm 1, \ell'N' \mp 1\rangle$  obtained during the transfer of one electron between M and R.

Since the system R has the same number of electrons  $N' = 4$  in the initial (I) and final (II) states, we will write our reaction in the subspace of the functions without transfer of charge between M and R. We take account of the configurations with charge transfer and the important resonance interactions of the operator  $H_I$ , following [13], as correlation corrections in the transition from the full Hamiltonian H to the effective Hamiltonian, which operates in the subspace of the functions with zero charge transfer (ZCT) between M and R and which has eigenvalues coinciding with the corresponding eigenvalues of the full Hamiltonian H. Let A be the subspace of the configurations with ZCT, let B be the additional subspace, and let  $P_A$  and  $P_B$  be the projectors onto these subspaces ( $P_A + P_B = 1$ ). We will write

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

The effective Hamiltonian  $H_{\text{eff}}$  for the term with energy  $E$  has the following form [13]:

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

where

$$R^B(E) = 1/(EP_B - H^{BB})$$

is the resolvent of the operator  $H^{BB}$ . With regard to Eqs. (10-14), for the matrix element  $H_{\text{eff}}$  we obtain:

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

### The Variation Method of Search for the Principal Term of the Effective Hamiltonian

The PES of the complex  $M + R$  is the smallest eigenvalue  $E = E(x, y)$  of the operator  $H_{\text{eff}}$ , which is obtained by solution of the equation:

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

where the variation function

$$\Psi = \sum_{kk'} C_{kk'} | kN, k'N' \rangle \quad \left( \sum_{kk'} | C_{kk'} |^2 = 1 \right) \quad (17)$$

is a function of the ZCT with unknown coefficients  $C_{kk'}$ . For an approximate value, instead of Eq. (17) we will consider the terms from the simpler problem:

$$E(\varphi) = \langle \Psi | H_{\text{eff}}(E_1^0) | \Psi \rangle, \quad (18)$$

where the variation function

$$\Psi = \Psi_1 \cos \varphi + \Psi_2 \sin \varphi \quad (19)$$

depends on one parameter  $\varphi$ ,

$$\Psi_1 = |^{2S+1}\Gamma N, ^1A_1 4\rangle, \quad \Psi_2 = |^{2S'+1}\Gamma' N, ^3A_2 4\rangle, \quad (20)$$

and the energy

$$E_1^0 = \langle \Psi_1 | H_0 | \Psi_1 \rangle = \langle ^{2S+1}\Gamma N | H_M | ^{2S+1}\Gamma N \rangle + E(^1A_1) \quad (21)$$

is the energy of the ground state of the Hamiltonian  $H_0$ . The desired PES is determined as the minimum with respect to  $\varphi$  for the expression

$$E(\varphi) = a \cos^2 \varphi + d \sin^2 \varphi + g \sin 2\varphi. \quad (22)$$

The expression (22) has a minimum at  $\varphi = \varphi_0$  and

$$\tan 2\varphi_0 = 2g/(a - d), \quad (23)$$

where

$$\begin{aligned} a &= \langle \Psi_1 | H_{\text{eff}}^0 | \Psi_1 \rangle, \quad d = \langle \Psi_2 | H_{\text{eff}}^0 | \Psi_2 \rangle, \\ g &= \langle \Psi_1 | H_{\text{eff}}^0 | \Psi_2 \rangle, \quad H_{\text{eff}}^0 = H_{\text{eff}}(E_1^0). \end{aligned} \quad (24)$$

From Eqs. (22)-(24) it follows that for  $g \neq 0$  the state  $\Psi_2$  with energy

$$E_2^0 = \langle \Psi_2 | H_0 | \Psi_2 \rangle = \langle ^{2S'+1}\Gamma' N | H_M | ^{2S'+1}\Gamma' N \rangle + E(^3A_2) \quad (25)$$

is admixed with the ground state  $\Psi_1$  of the Hamiltonian  $H_0$ . The spatial symmetry  $\Gamma$ ,  $\Gamma'$  and the spins  $S$ ,  $S'$  are determined from the condition in which the  $\Psi_1$  and  $\Psi_2$  functions have the same spatial and spin symmetry.

We write the PES of the ground state with regard to Eqs. (15, 22-24) in the following form:

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

where the first two contributions are due to the admixture of the triplet term with the ground singlet term, while the contributions from Eq. (22) are incorporated in the last term. The minimum of the  ${}^3A_2$  term is close to the maximum of the  ${}^1A_1$  term in the region of the reaction barrier [see Fig. 2 and Eqs. (5)]. Therefore, if only the first two terms of Eq. (26) are taken into account, the size of the barrier for the reaction  $I \rightarrow II$  decreases if  $\varphi_0$  differs from zero.

#### Comparative Assesments of the Catalytic Activity of the Complexes CoTPP and MnTPP

We will compare the values of the parameter  $\tan 2\varphi_0$ , characterizing the catalytic activity, for the complexes of Co-tetraphenylporphyrin (CoTPP) and Mn-tetraphenylporphyrin (MnTPP), of which the former catalyzes the reaction  $I \rightarrow II$  while the latter is an analog of the catalytically inactive  $d^5$  complexes Fe(III)TPP and MnPc. We took the energies of the terms for the catalyst, required for determination of  $\tan 2\varphi_0$ , from experimental data, or we obtained them from calculation with full allowance for the interaction of the  $d$  electrons of the metal.

Let us consider the Hamiltonian  $H_M$  in the crystal field model in the  $d$  approximation, where the characteristics of the  $Mn^{2+}(3d^5)$  and  $Co^{2+}(3d^7)$  ions are determined only by their  $d$  electrons. The  $H_M$  matrices with the inclusion of the coulombic interaction in the  $d^N$  shell in the  $C_{4v}$  symmetry field (the symmetry field of the ligands in our complexes) were constructed in [14]. The splitting of the levels in the field of the ligands is described by the parameters  $X$ ,  $Y$ , and  $Z$ , while the coulombic interaction of the  $d$  electrons is considered the same as in the free ion and is determined by the Racah parameters  $A$ ,  $B$ , and  $C$ . The splitting parameters for CoTPP are as follows [15]: Co,  $X = 1.3$  eV,  $Y = 2$  eV, and  $Z = -0.5$  eV. In the case of MnTPP we reduce these values by a factor of 1.3: Mn,  $X = 1$  eV,  $Y = 1.54$  eV, and  $Z = -0.38$  eV. Such a choice of parameters takes account of the fact that the  $10 Dq$  values (a parameter analogous with  $X$ ) in octahedral complexes are on the average 1.3 times smaller for the complexes of Mn(II) than for the complexes of Co(II) [16].

According to [15], the ground state of CoTPP has  ${}^2A_1$  symmetry, and  $\Psi_1$  therefore relates to  ${}^2A_1 \otimes {}^1A_1 = {}^2A_1$  symmetry. The lowest state of CoTPP in energy which makes it possible to obtain the same symmetry for  $\Psi_2$  is the  ${}^4B_2$  state. (In the  $M + R$  system, which has  $C_{2v}$  symmetry, the  ${}^4B_2$  state is reduced to  ${}^4A_2$ , and then  ${}^4A_2 \otimes {}^3A_2 = {}^2A_1 \otimes {}^4A_1 \otimes {}^6A_1$ .) According to [17], the ground state of MnTPP has  ${}^6A_1$  symmetry; the same symmetry is characteristic of  $\Psi_1$  and  $\Psi_2$  ( ${}^6A_1 \otimes {}^1A_1 = {}^6A_1$ ). The lowest excited term of MnTPP in energy, which leads to  $\Psi_2$  ( ${}^6A_1$ ), has  ${}^4A_2$  symmetry.

We determine  $\tan 2\varphi_0$  by means of Eq. (23). On the assumption that the correlation corrections to the diagonal matrix elements of  $H_0$  in the expressions for  $a$  and  $d$  [the sums with respect to  $qq'$  in Eq. (15)] are approximately identical and are therefore compensated during calculation of the difference ( $a - d$ ) we obtain the following value:

$$a - d = E_M^0({}^{2S+1}\Gamma) - E_M^0({}^{2S'+1}\Gamma') \equiv -\Delta E_M^0. \quad (27)$$

For CoTPP, according to experimental data [15], we obtain:

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

For MnTPP the energies of the  $E_M^0$  terms were calculated in the following way. By means of the matrix elements of the Hamiltonian  $H_M$  given in [14] with the values of  $X$ ,  $Y$ , and  $Z$  determined above and the Racah parameters  $B = 0.1$  eV and  $C = 0.5$  eV from [16] we took the interaction of the  $d$  electrons fully into account, realizing the diagonalization of the respective matrices, and obtained the energies of the  ${}^4A_2$  and  ${}^6A_1$  terms. As a result the desired difference in energies is equal to:

$$\Delta E_{Mn}^0 = E_{Mn}^0({}^4A_2) - E_{Mn}^0({}^6A_1) = 1.7 \text{ eV.}$$

During determination of  $g$  by means of Eqs. (15, 20, 24) we first obtained the number of nonzero terms in the sums with respect to  $qq'$ . This number is equal to the number of intermediate states ( $qq'$ ) of the required symmetry and spin in the  $d^6$  and  $d^8$  shells for CoTPP and the  $d^4$  and  $d^6$  shells in the case of MnTPP. With due regard to the rule of the combination of spins and the explicit form of the operator  $H_I$  we come to the conclusion that the symmetry of these levels is  ${}^3B_1$  ( $i = 1, 2$ ) for CoTPP and  ${}^5B_1$  for MnTPP ( $C_{2V}$  symmetry). The number of states with  ${}^{2S+1}B_i$  symmetry is twice the number of  ${}^{2S+1}E$  states ( $C_{4V}$  symmetry), while the number of these states according to [14] is:  $N_{Co} = 15$ ,  $N_{Mn} = 2$ . The number of nonzero terms in the expression for  $g$  according to Eq. (15) is  $\tilde{N}_{Co} = 30$  for CoTPP and  $\tilde{N}_{Mn} = 4$  for MnTPP. Disregarding the weak dependence of the parameter  $g$  on the coordinates ( $x, y$ ), we determine its value by means of the mean-value theorem:

$$g = \sum_{v \in B} \frac{\langle kN, k'N' | H_I | v \rangle \langle v | H_I | lN, l'N' \rangle}{E - E_v} \approx -\tilde{N}_{Co} \frac{b^2}{\Delta E_g}$$

where the summation is performed among the states with electron transfer between the metal and the reagents. For the average energy of the states with electron transfer we take the value  $\Delta E_g \approx 10$  eV, and for the average resonance parameter we use  $b \approx 1$  eV. (This value agrees with the values of the resonance parameters between the AO of the metal and the reagents with overlap integrals of  $S \approx 0.05-0.1$  [16].) Then (with  $\tilde{N}_{Co} = 30$ ) we obtain  $g \approx -3$  eV. Finally, by means of Eqs. (22) and (23) we construct the curve for the potential along the reaction path with the obtained value of  $g$  and find (Fig. 2) that the activation energy  $\Delta E_{theor}$  (CoTPP) = 0.22 eV.

We will compare the  $\tan 2\varphi_0$  values for the two complexes. Since the denominator of the expression for  $\tan 2\varphi_0$  in the case of MnTPP (a - d) is 10 times larger than in the case of CoTPP while the number of terms in the numerator is seven times smaller, determination in the region of the reaction barrier gives:

$$(\tan 2\varphi_0)_{MnTPP} / (\tan 2\varphi_0)_{CoTPP} \approx 10^{-2} \quad (28)$$

The obtained ratio of the  $\tan 2\varphi_0$  parameters indicates that the catalytic activity of the MnTPP must be significantly lower than that of CoTPP. The ground state of Fe(III)TPP, like that of MnTPP, has a total spin of  $S = 5/2$ ; determination of the  $\tan 2\varphi_0$  parameter for Fe(III)TPP, which we made in the same approximations, leads to the same result as for MnTPP. This is consistent with the absence of catalytic activity in the Fe(III)TPP complex in the investigated reaction, discovered in [2]. For the other inactive  $d^5$  complex MnPc [2] there is no direct information on the spin of the ground state of the catalyst under the reaction conditions. In the MnPc crystal the principal term is  ${}^4A_2$  [18]. The excited term  ${}^6A_1$  has an energy of  $\sim 0.075$  eV and may become the principal term during passage of MnPc into solution. This suggestion is based on the fact that the existence of MnPc in the  ${}^4A_2$  state in the crystal is due to additional splitting of the terms of the  $d$  electrons of the Mn atom, due to the nitrogen atoms of the neighboring MnPc molecules [18]. The additional splitting disappears during passage into solution. In this case the value of  $\tan 2\varphi_0$  for MnPc will be the same as for MnTPP, and this leads to the conclusion that MnPc is inactive in the reaction, in accordance with experiment [2].

It should be noted that the admixture of the excited triplet state (the  $a_1^2 b_1 b_2$  configuration) in the principal term of the reagents increases the population of the antibonding orbital. From the standpoint of vibronic theory [7] this can be interpreted as a change in the vibronic instability, and this leads to a decrease in the height of the reaction barrier. The method of admixture (inclusion) of the excited states proposed in the present work differs from the theories in [5, 7], beginning with the method of construction and terminating in the selection and inclusion of the interaction of the electronic configurations. In terms of the proposed approach with an effective scheme for the inclusion of the electronic correlations it was possible to relate the catalytic activity of the metal complexes in the reaction to their optical and magnetic characteristics, which are determined by the  $d$  electrons of the metal.

In contrast to calculation for the combined system by the LCAO-MO scheme, in the proposed method both subsystems (the reagents and the catalyst) can be calculated separately with any degree of completion. In particular, for the metal of the catalyst it proved necessary to

conduct the calculation with full regard to the interaction of the d electrons in order to obtain terms with the correct spin multiplicity. In the LCAO-MO scheme the inclusion of the metal in the combined system in a high-spin state involves considerable difficulties, which are often circumvented with violation of the rule of occupation of the orbitals with lowest energy.

#### LITERATURE CITED

1. H. Hogeveen and B. J. Nusse, "Rhodium(I) catalyzed valence isomerization of quadricyclanes," *Tetrahedron Lett.*, 1973, No. 38, 3667-3670.
2. J. Manassen, "Catalysis of symmetry restricted reaction by transition metal complexes. The importance of the ligand," *J. Catal.*, 18, No. 1, 38-45 (1970).
3. K. S. Bishop, "Transition metal catalyzed rearrangements of small ring organic molecules," *Chem. Rev.*, 76, No. 4, 461-486 (1976).
4. V. I. Labunskaya, A. D. Shebaldova, and M. L. Khidekel', "Catalysis of symmetry-forbidden reactions," *Usp. Khim.*, 43, No. 1, 3-34 (1974).
5. F. D. Mango, "Molecular orbital symmetry conservation in transition metal catalysis," *Adv. Catal.*, 20, 291-325 (1969).
6. M. Zerner and M. Goutermann, "Porphyrins. 4. Extended Hückel calculations on transition metal complexes," *Theor. Chim. Acta*, 4, No. 1, 44-63 (1966).
7. I. B. Bersuker, "Problems of molecular instability, vibronic reactivity, and activation of small molecules during coordination," *Zh. Fiz. Khim.*, 59, No. 5, 1099-1111 (1985).
8. M. C. Böhm, "On the quantum chemical origin for the nonvalidity of Koopmans' theorem in transition metal compounds," *Theor. Chim. Acta*, 61, No. 6, 539-558 (1982).
9. R. Hoffmann and R. B. Woodward, "Selection rules for concerted cycloaddition reactions," *J. Am. Chem. Soc.*, 87, No. 9, 2046-2048 (1965).
10. I. A. Misurkin and A. A. Ovchinnikov, "Electronic structure and properties of polymeric molecules with conjugated bonds," *Usp. Khim.*, 46, No. 10, 1835-1870 (1977).
11. H.-D. Martin, G. Heller, E. Haselbach, and Z. Lanyjova, "Quadricyclanes. 1. Photoelectron spectra and electronic structure," *Helv. Chim. Acta*, 57, No. 2, 465-472 (1974).
12. R. B. Turner, P. Goebel, B. J. Mallon, et al., "Heats of hydrogenation. 8. Compounds with three- and four-membered rings," *J. Am. Chem. Soc.*, 90, No. 16, 4315-4322 (1968).
13. R. MacBinny and B. Sutcliffe, *Quantum Mechanics of Molecules* [Russian translation], Mir, Moscow (1972).
14. J. Otsuka, "Electronic interaction of  $d^n$  system in tetragonal fields," *J. Phys. Soc. Jpn.*, 21, No. 4, 596-620 (1966).
15. W. C. Lin, "d-Orbital energy and low-lying excited states of cobalt porphyrins," *Inorg. Chem.*, 15, No. 5, 1114-1118 (1976).
16. I. B. Bersuker, *Electronic Structure and Properties of Coordination Compounds* [in Russian], Khimiya, Leningrad (1976).
17. C. J. Weschler, B. M. Hoffmann, and F. Basolo, "Synthetic oxygen carriers. A. Dioxygen adduct of manganese porphyrine," *J. Am. Chem. Soc.*, 97, No. 18, 5278-5285 (1975).
18. C. G. Barraclough, A. K. Gregson, and S. Mitra, "Interpretation of the magnetic properties of manganese(II) phthalocyanine," *J. Chem. Phys.*, 60, No. 3, 962-968 (1974).