

QUANTUM CHEMICAL AND STATISTICAL-THERMODYNAMIC STUDIES OF EQUILIBRIA AND RATES

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Abstract - A review of the main results from our laboratory for the period 1969-1982 is presented. In the introductory part, allowed and forbidden processes are discussed from the point of view of constants of motion. Specific suggestions are presented as to how to make forbidden processes allowed. In addition to energy forbiddenness, entropy forbiddenness is also mentioned. In the section on equilibria attempts to locate minima of potential energy surfaces (PES), and statistical-thermodynamic calculations of equilibrium constants for common and van der Waals molecules, are summarized. Then information follows on the location of saddle points on PES, reaction coordinates and statistical-thermodynamic calculations of rate constants of elementary reactions. The final section deals with studies of catalytic reactions.

INTRODUCTION

About 25 years ago we started our work on the theory of chemical reactivity. The period up to 1969 was summarized in connection with a meeting held in Menton (Ref. 1). The present paper covers approximately the period between 1969 and 1982 and deals with statistical-thermodynamic treatments of equilibria and rates, with stationary points of potential energy surfaces (PES), and with catalysis. Both, common and van der Waals (vdW) molecules have been investigated. (For previous general reviews see Ref. 2 & 3; moreover a review on catalysis (Ref. 4), a book (Ref. 5) and a review (Ref. 6) on vdW molecules and another review on a related subject (Ref. 7) have appeared.)

It is the purpose of this article to summarize the results obtained in our laboratory including those which appeared as products of cwork with the groups of Dr. M. Urban and Dr. I. Hubač from Bratislava. Scope limitation prevents a systematic citation of works from other laboratories.

GENERAL REMARKS

Selection rules based on constants of motion. A generally applicable selection rule (Ref. 8) is available for chemical reactions of all types and for scattering processes. According to this rule a process is allowed (i.e. connected with a relatively low or negligible energy barrier separating valleys

of reactants and products) if the eigenvalues of all the operators commuting with the Hamiltonian remain constant when the system passes from reactants to products. In other words, there exist quantities (named constants or integrals of motion), the value of which remain unchanged during the chemical reaction. Angular momenta and spins of electrons are the most important quantities of this sort (conservation of these quantities is a consequence of the assumed homogeneity and isotropy of space (Ref. 9)). Essentially, the conservation law originates from 19th century physics. The outstanding feature of the quantum mechanical formulation is that symmetry operators also belong to the system of operators commuting with the Hamiltonian. Therefore, conservation of state and orbital symmetries is a natural consequence of this law. The satisfaction of the conservation law sometimes requires a transition, which is connected with the crossing of states. Such a transition is associated with a relatively high energy barrier separating reactants and products: the respective process is thermally forbidden. As a matter of fact symmetry and not orbital angular momenta is used for establishing whether the process under study is allowed or forbidden; the point is that angular momenta cease to be good quantum numbers for systems larger than diatomics.

How to make forbidden processes allowed? The only possibility we have is to pass from the PES where the process is forbidden, to another, related PES, where the process is allowed (Ref. 10). The possibilities are as follows (Ref. 10 & 11): 1. transition to an electronically excited PES (of the same or higher spin multiplicity), 2. transition to the PES of the respective radical ions, 3. transition to the PES of the system under study exposed to external force field (mainly to the electric field (Ref. 12 & 13)), 4. transition to the PES of vdW associates of one of the reactants, 5. transition to the PES of a complex between the reactants and a catalyst. The possibilities 1. to 5. together with various combinations thereof represent a rather powerful tool for the preparation of most different systems.

Entropy forbidden processes (Ref. 14 & 15). The previous paragraph dealt with energy forbidden processes. In chemistry we are usually concerned with bulk reactivity. Therefore, the Gibbs activation energy rather than the activation energy is decisive for the reaction course. For the majority of chemical reactions the activation enthalpy, ΔH^\ddagger , is larger than the $T\Delta S^\ddagger$ term. The value of ΔH_0^\ddagger determines whether the process is energy allowed or forbidden. Processes can occur that are energy allowed but the formation of the activated complex requires an involved structural adjustment of reactants connected with a large activation entropy decrease (entropy forbidden processes). This kind of forbiddenness can be overcome if a sufficiently strong vdW molecule can be formed from the reactants, possessing a structure that is close to the structure of the activated complex. The entropy lost, connected with formation of the vdW molecule, is compensated by the energy released during the formation of the vdW molecule. The transition between the vdW molecule and the activated complex is mostly easy from the viewpoint of both, the energy and the entropy.

EQUILIBRIA

Location of minima on potential energy surfaces. The period of pioneers started in the late sixties. At that time, Pulay (16) in Budapest, McIver and Komornicki (17) in Buffalo and Panciř (18) in Prague dealt with molecular geometry optimization, based on the potential energy gradient. During the seventies the gradient procedure was introduced into a broad variety of quantum chemical methods ranging from EHT (Ref. 19), via CNDO/2, INDO, MINDO/2 (Ref. 18 & 20), and PCILO (Ref. 21) to ab initio (Ref. 22 & 23). The force constant matrix (the Hesse matrix) has been used for establishing the nature of the located stationary points (local minima, saddle points). At present optimization procedures are incorporated in the majority of important semiempirical and nonempirical methods available from computer program exchange centres.

Statistical-thermodynamic treatment. The procedures for evaluation of equilibrium and rate constants of gas-phase processes are much alike and, therefore, their important features can be described together. The treatment consists of the following four steps: 1. location of stationary points on the PES, 2. calculation of ΔH_0^0 (for equilibria) or $\Delta H_0^{0\ddagger}$ (for rates), 3. quantum chemical calculation of molecular constants needed for evaluation of equilibrium and rate constants in terms of partition functions, 4. correction for quantum mechanical tunneling. A few comments follow on items 1-3; the tunneling correction is mentioned in the next section.

The location of local minima is mostly a straightforward process. However, the difficulty increases rapidly with the number of atoms of the optimized structure. The location of saddle points is much more tedious (vide infra). The diagonalization of the Hesse matrix makes the distinction between minima and saddle points easy. Again, its evaluation with larger systems is time-consuming but the force constants are anyhow necessary in order to be able to perform the Wilson FG analysis.

The energy terms in standard expressions for evaluation of equilibrium and rate constants mostly represent the critical quantities. Therefore as accurate as possible ΔH_0^0 ($\Delta H_0^{0\ddagger}$) values are required. The lack of reliability of semiempirical MO methods has discouraged us from using them systematically. Nonempirical calculations are desirable if one aims at absolute values of equilibrium and rate constants. Analysis of more extensive portions on the PES can be based on the DZ type of calculation (e.g., 4-31G or 3-21G). The located minima should be reoptimized on the DZ+P level (e.g., 4-31G⁺ or 4-31G⁺⁺). The neighbourhood of these minima can be investigated again on a simpler level (DZ) in order to get the values necessary for the evaluation of quadratic force constants. The SCF energies obtained for the minima must be corrected for the zero-point energy and for the correlation error. As to the latter we have good experience with both, the MB-RSPT and CEPA procedures (for more details, see Ref. 24). For semiquantitative purposes the second order MB-RSPT values are sufficient; for more quantitative studies contributions up to the fourth order are desirable. For rough estimates, in

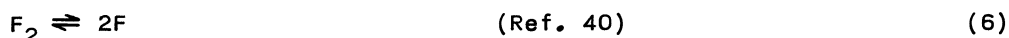
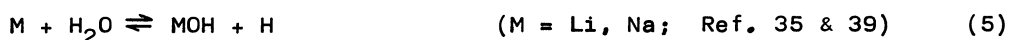
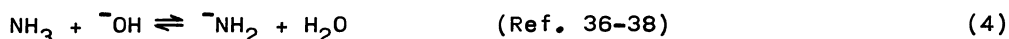
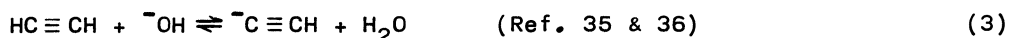
some special connections, it is possible to use the semiempirical EPCE-F20 method (Ref. 25-27).

The molecular constants needed for evaluation of factorized partition functions are mostly generated at the DZ level (for applicability of semiempirical methods, see Ref. 28). Rigid rotor, harmonic oscillator and ideal gas approximations have been used throughout our calculations. The evaluation of the vibrational partition functions represents the demanding step; the Wilson FG analysis requires a knowledge of the complete matrix of the force constants. In recent calculations of the vibrational modes correlation energy was included (Ref. 29). The frequencies obtained for the normal vibrational modes serve not only for the evaluation of the vibrational partition function, this function being especially sensitive to the accuracy of the low energy modes, but also for calculating the zero-point energy for which, on the contrary, the high energy modes are decisive. The imaginary mode associated with the negative eigenvalue of the Hesse matrix can be used for estimating the tunneling correction, *vide infra*. The role of the electronic partition function was discussed (Ref. 30).

An extensive set of equilibria has been studied. Originally ΔH_0^0 calculations were based on semiempirical methods of the NDO type (Ref. 31-33). The lack of confidence in the semiempirical methods represented the main driving force for investigation of nonempirical calculations. Typical equilibria studied are the following:



(and twelve related equilibria involving first row hydrides, AH_2 , AH_3 , and AH_4 , and their positive ions (Ref. 34))



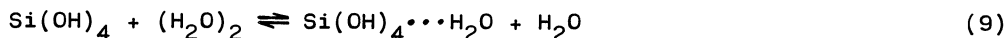
On the whole, it is possible to say that the DZ+P level for energy calculations ($\Delta E^{\text{SCF}} + \Delta E^{\text{CORR}}$) together with molecular constants generated on the DZ level represent, in the majority of cases, a good basis for obtaining equilibrium constants of nearly chemical accuracy (Ref. 41). There are some exceptions concerning mainly weak intermolecular complexes (*vide infra*) and equilibria including negatively charged species (Ref. 36-38) (cf. Ref. 42). Calculations on these species are more demanding. Extensive attention has been given by P. Čársky and I. Hubač to some problems concerning the calculation of correlation energy by means of the MB-RSPT (for a summary see Ref. 44 & 45).

Formation of vdW systems (Ref. 46 & 47). These systems are mostly formed by downhill interactions of two or more closed-shell systems. Except for special cases, accurate calculation of interaction energy is more demanding than with common molecules. In general, the correlation energy contribution must not be neglected and, in order to have a high enough yield, it has to be calculated for at least the (DZ+2P) SCF wave function. One of the two polarization functions has to be diffuse, otherwise the intersystem correlation energy cannot be described properly. Calculations with basis sets of this size are still limited to small systems. In model calculations for biological problems, reductions have to be introduced concerning both, the SCF and correlation parts of the total energy change. The following expression offers reasonable, relatively cheap, estimates for ΔE including those for relatively large systems (Ref. 47):

$$\Delta E = \Delta E^{\text{SCF}} + \text{BSSE} + E^{\text{D}} \quad (7)$$

where ΔE^{SCF} is obtained for the DZ or DZ+P type of basis set, BSSE is the basis set superposition error according to Boys and Bernardi (48) and E^{D} is the dispersion energy, usually estimated on the basis of some semiempirical formula. For more details, see Ref. 47.

Statistical thermodynamic treatment of the formation (Ref. 5 & 6) of vdW molecules (e.g., Eq. 8) and of exchange reactions (e.g., Eq. 9) was performed (Ref. 49 & 50)



The ΔG^0 values of formation of vdW systems are, at laboratory temperatures, significantly influenced by the entropy changes.

The influence of local electric fields has been studied with hydrogen bonded complexes of the type $(\text{HX} \cdots \text{HX})\text{M}$, where X is either F or Cl and M is Li^+ , Na^+ or Mg^{2+} (Ref. 51). In connection with studies on zeolites, the electric field of an extensive neighbourhood was simulated by point charges (Ref. 52).

Intramolecular discriminatory interaction (due to short-range forces) has been investigated for 1,2-difluorohydrazine (Ref. 53). Three forms have been taken into consideration, the meso-form and the two optically active forms. The discrimination energy amounts to 16 kJ/mol.

RATES

Location of saddle points on PES. The empirical BEBO relationship of the form $\exp[-a(r_{\text{AB}} - r_{\text{AB}}^0)] + \exp[-a(r_{\text{BC}} - r_{\text{BC}}^0)] = 1$ has been used for finding the transition states (saddle points) of collinear reactions, $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, from a small number of data of the respective potential surfaces. The util-

ity of the procedure, even in searches for transition states of more complex reactions, has been shown by means of the 4-31G surface for the process $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$ (Ref. 54).

Reaction coordinates. Introduced reaction coordinates, although not quite satisfactorily defined, represent a powerful tool for analyzing the PES. This is particularly true for finding all the stationary points on a given surface. The reaction coordinate can be found by a constrained minimization in all directions perpendicular to the driving force. Unfortunately, the choice of an internal coordinate as the driving force results in chemical hysteresis. As a consequence of this hysteresis, the reaction coordinate starting from reactants differs from that starting from products and neither passes through activated complex. The most substantiated "intrinsic reaction coordinate" (Ref. 55) passes exactly through the activated complex, but its analysis must start from this point. This is an unfavourable circumstance because such a coordinate cannot be used for finding the activated complexes. In our laboratory a coordinate was introduced (Ref. 56) with a constraint requiring parallelity between the potential energy gradient and a selected eigenvector of the Hesse matrix. This coordinate can start from a minimum on the PES, passes exactly through the activated complex and approaches the intrinsic coordinate in the vicinity of the stationary points. The coordinate was tested on the formaldehyde-hydroxycarbene rearrangement (Ref. 57).

The concept of reaction coordinate was generalized (Ref. 58) with regard to the possibility of treating the multidimensional PES. The second order reaction coordinate was defined as the optimal two-dimensional cut of the given PES with respect to two independent driving forces. Such a treatment can be conveniently used, for example, for simultaneous study of two parallel reactions and concertedness of the reactions. This coordinate has been used in our laboratory in connection with a topological procedure outlined in the next paragraph.

The topological procedure was developed, programmed and tested by J. Pancíř (59-61). Within the framework of this procedure, chemical reactions are described in terms of processes in which some of the original bonds are broken and some others are newly formed. In other words, molecules are considered as sets of isolated bonds and reactions are due to the electron flow from regions of broken bonds to regions of newly created bonds. The wave function and the respective Hamiltonian matrix elements of the reacting molecule anywhere between the reactants (R) and the products (P), are expressed as linear combinations of atomic orbitals and matrix elements of R and P. The respective expansion coefficients represent a basis for the space where the energy hypersurface is constructed. For the i -th atomic orbital, χ^i , of the supersystem, with a structure somewhere between R and P, it is possible to write:

$$\chi^i = c_R^i \chi_R^i + c_P^i \chi_P^i \quad (10)$$

where χ_R^i and χ_P^i are the i -th atomic orbitals of R and P and c^i are the expansion coefficients. As the formed and broken bonds are located in different parts of space, the expansion coefficients have to satisfy the orthonormalization condition. Using a geometric substitution, the following formula results:

$$\chi^i = \cos \varphi^i \chi_R^i + \sin \varphi^i \chi_P^i \quad (11)$$

When introducing (11) into the expression for the matrix elements of the reacting supersystem, it is possible to express them in terms of known elements for R and P, multiplied by goniometric functions of φ^i . The energy of the reacting supersystem is investigated in the topological space spanning the reaction angles, φ^i . The procedure has been elaborated on three levels of sophistication: HMO, Hartree-Fock SCF and the LCI level. In the latter, singly and selected doubly excited configurations are considered. Localized orbitals have been used. There are two factors which make the topological analysis of energy hypersurfaces and reaction coordinates most economic. First, only bonds directly participating in the process under study are considered explicitly, all others being included in the core. Second, the dimension of the topological hypersurface is much smaller than the dimension of the corresponding geometrical hypersurface ($3n - 6$ in the latter case, where n is the number of atoms) and is given by the number of reaction centres, i.e. the number of reaction angles, φ^i .

Statistical-thermodynamic treatment. On the basis of the Eyring absolute rate theory a series of reactions of the type $A + BC \rightarrow AB + C$ (A and BC correspond to H, F, HF, H₂, CH₄) was studied (Ref. 30). The best accessible geometries and energies of activated complexes originated from published studies (see Ref. 30). At least the DZ+P basis set was used and a large portion of the correlation energy was included. Vibrational frequencies, needed for the zero-point energies and vibrational partition functions, were either obtained from the reported potential surfaces or evaluated from the SCF (4-31G) calculations (Ref. 62). The role of the electronic partition function was discussed. In order to obtain good agreement between calculated and observed rate constants a correction for quantum mechanical tunneling has to be considered for reactions including hydrogen atoms (Ref. 63).

Catalysis

The presence of heavier atoms in catalysts makes the theoretical determination of reactive intermediates and the analysis of reaction coordinates a very involved task. On the basis of similarities between photochemical, radical-ionic and catalytic reactions, a model procedure was developed, named the approximation of isolated substrate (Ref. 64). Instead of explicitly dealing with a substrate-catalyst complex, only the properly perturbed substrate is treated semiempirically. Specifically, for the catalytic oxidation of ethylene (and propylene) on silver, only interactions between ethylene (propylene) and the oxygen radical anion and the oxygen dianion were treated quantum chemically. This approach permitted us to interpret the reaction mechanism and to understand the qualitative differences in the

behaviour of ethylene and propylene (Ref. 65 & 66). The catalytic decomposition of cyclopropane was interpreted along similar lines (Ref. 67).

The sorption properties of bulk and surface structural units ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$, $\equiv\text{Si}-\text{O}-\text{Al}^-\equiv$, $(\text{OH})_3\text{SiOH}$) of quartz and zeolites have been studied nonempirically and the intersystem component of the correlation energy change has been estimated by means of the dispersion energy (Ref. 49 & 68). The ability of the individual groups to destroy a model hydrogen bond (e.g., in $(\text{H}_2\text{O})_2$) has been calculated. The role of strong local electric fields (e.g., in cavities of zeolites) on the course of chemical transformation has been pointed out.

Common features of enzymic processes were discussed (Ref. 14). The main attention was paid to the role of vdW forces (Coulomb attraction, exchange and Coulomb repulsion) in the rapid stages of enzyme-substrate interactions, to the role of entropy and strong local electric fields and, finally, to the special structural arrangement of the active sites.

Let us close this section by a note on a recent application of the topological procedure to the analysis of a model interaction between a cluster of 24 sodium atoms (two layers of 3×4 atoms) and a hydrogen molecule (Ref. 69). Surfaces (100), (110), (111) and (112) derived from clusters of simple cubic, body-centered cubic and face-centered lattices were studied. A simple selection rule was derived that permits estimation of the structure of the surface complex between H_2 and Na_{24} .

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