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Transition State Modeling for Catalysis

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THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded in order to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

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A. Dedieu, F. Hutschka, and A. Milet

Preface

This volume contains contributions from the speakers at the Symposium on "Transition State Catalysis in Computational Chemistry," sponsored by the Division of Computers in Chemistry at the National Meeting of the American Chemical Society in Dallas, March 30–April 2, 1998. Most of the papers are by invited speakers. The European community, which is very strong in the area, is well represented in this international symposium.

The symposium was unique, and the volume is unique in the same way. This is because it includes both homogeneous and heterogeneous catalysis, including organometallic catalysts, biological systems, zeolites and metal oxides, and metal surfaces. Furthermore, the emphasis is on actual *transition state modeling*, in contrast to the much more widely studied topic of precursor binding.

Computational chemistry is making explosive inroads on many areas of practical concern, and it is becoming an important tool for catalyst design. We believe that this symposium and volume catch the cutting-edge field of transition state modeling for catalysis in its infancy. These are the seminal studies that will set a tone for the next decade and beyond. We hope the book will be of great interest to a broad group of industrial and academic chemists worldwide.

All contributions to the volume received peer review, coordinated by the editors. Peer review for the three chapters for which one or both editors is a coauthor was arranged by Anne Wilson of ACS Books. We would like to take this opportunity to thank Anne Wilson for this and also for making our interactions with the publisher smooth and enjoyable at every step of the planning and production of this volume.

The editors were also the symposium organizers. We were very pleased to be assisted in organizing the conference by the following International Advisory Board of experts in the field: Gernot Frenking, Gabor Náray-Szabó, Vern L. Schramm, Rutger A. van Santen, and Arie Warshel.

We would like to close by thanking the authors for adhering remarkably well to deadlines and thanking the referees for providing speedy review. Copies of the proceedings papers were due 2.5 weeks before the symposium, and the book was completed only 4 weeks after the conclusion of the symposium.

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Dedicated to
Eiko, Jane, Sara, and Stephanie

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INTRODUCTION

INTRODUCTION

Chapter 1

Quantum Catalysis: The Modeling of Catalytic Transition States

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INTRODUCTION

We present an introduction to the computational modeling of transition states for catalytic reactions. We consider both homogeneous catalysis and heterogeneous catalysis, including organometallic catalysts, enzymes, zeolites and metal oxides, and metal surfaces. We summarize successes, promising approaches, and problems. We attempt to delineate the key issues and summarize the current status of our understanding of these issues. Topics covered include basis sets, classical trajectories, cluster calculations, combined quantum-mechanical/molecular-mechanical (QM/MM) methods, density functional theory, electrostatics, empirical valence bond theory, free energies of activation, frictional effects and nonequilibrium solvation, kinetic isotope effects, localized orbitals at surfaces, the reliability of correlated electronic structure calculations, the role of *d* orbitals in transition metals, transition state geometries, and tunneling.

Computational chemistry has achieved great strides in recent years, and it has become a strong partner with experimental methods, displacing purely analytic theory almost completely. The essential element in computational chemistry is the use of very general theoretical frameworks that can be applied broadly across a number of fields. Examples are molecular orbital theory, molecular mechanics, transition state theory,

classical trajectories, and the Wentzel-Kramers-Brillouin method. As the techniques of these fields are developed, they can be applied across broad ranges of problems in chemical structure and reactivity. When this pack of techniques is used to attack a herd of problems, it is only natural that attention is first focussed on the easiest ones. As these begin to succumb, computational chemistry sets its sights on more recalcitrant targets. Thus computational chemistry has been very successful for calculating structures and energies of small molecules, structures and energies of large molecules, and properties of simple reactions of these molecules. An emerging competency is the treatment of complex reactions involving catalysts. A critical element in this endeavor is the ability to directly model the transition state.

Systems of interest range from heterogeneous catalysis, through transition metal complexes, both classical and organometallic, to bioinorganic chemistry of enzymes and enzyme mimics. Often a reasonably accurate structure and a semi-quantitative relative energy for possible transition states can be helpful in pointing the way to the correct reaction mechanism. Knowledge of the mechanism is important as it directs the thinking about how to modify the reaction under study or how to create a new reaction. In many cases experimental work will provide an approximate relative free energy for the key or rate-determining transition state, but ascertaining its structure from experimental data is much more difficult. Here, theory can help. In fact conventional quantum chemistry is arguably at its best when determining structures.

Catalysts are molecular devices that are able to perform complicated chemical manipulations on individual molecules. Although they are technologically attractive entities, engineering them for a given task is a challenge that is only slowly coming within reach. Whereas it is possible to efficiently design and build macroscopic machines using classical mechanics, it is quite another matter to do so with individual atoms and molecules, which behave according to the laws of quantum mechanics. Thus quantum mechanical modeling methods play a prominent role in catalyst modeling and computational catalyst design.

An appropriate model of a catalytic system is, in most cases, quite complicated and consists of many atoms. Owing to their relative mathematical simplicity molecular mechanics and classical trajectory studies may be applied with explicit consideration of all components; however full models of practically important systems are beyond the scope of quantum mechanical methods. A more and more popular approach to quantum mechanical modeling is partitioning of the catalytic system (substrate interactions with an enzyme, zeolite pore, solid surface, or solvent) into various regions (1-8). The active site or central machinery (C) is surrounded by a polarizable environment (P) which is embedded in a non-polarizable region (N) and solvent (S). Some regions may overlap and others may be dropped completely from the model, depending on the degree of sophistication of the treatment and their effect on the process. A very great variety of implementations are possible, differing in details, and we will elaborate on some variations at appropriate points in this article.

The minimum-size active site model (C) should be composed of those atoms that undergo chemical changes during catalysis, i.e., participate in the bond(s) that will be cleaved or formed during the process. For example, in enzyme catalysis by serine proteases, which hydrolyze peptide bonds, C must contain at least the =N-C=O moiety of the peptide bond, the -OH group of the attacking serine, and the proton acceptor imidazole ring of the nearby histidine. For systems where electronic excitation or electron transfer plays a role (e.g., heme proteins) the minimum-size active site may contain several dozen atoms. Reactions at metal surfaces require considering a large number of metal atoms in order to converge the work function and the tendency to create electron-hole pairs. Reactions in high-dielectric-constant solvents, such as water, require considering a large number of solvent molecules in order to obtain converged electrostatic energies.

Transition State Theory

The rate constants for reactions in the condensed phase can be written (9)

$$k = \kappa \frac{k_B T}{h} \exp[-\Delta G^{\ddagger,0}(T)/RT] \quad (1)$$

where $G^{\ddagger,0}$ is the standard-state free energy of activation that reflects the probability of reaching the transition state, R is the molar Boltzmann constant, and κ is the transmission coefficient (10) which contains dynamical effects. $G^{\ddagger,0}(T)$ reflects a compromise of quasiequilibrium energetic and entropic effects; κ reflects the probability of a trajectory recrossing the transition state, and it may include effects variously labeled as dynamic or nonequilibrium effects or friction. The transmission coefficient must also include quantum effects on the reaction coordinate motion, which is otherwise intrinsically classical in transition state theory (11). In conventional transition state theory (12), $G^{\ddagger,0}(T)$ is calculated at the saddle point of the Born-Oppenheimer potential energy surface (PES) for the reaction, whereas in variational transition state theory it is calculated at the maximum of the free energy of activation profile (5,9,12,13), which is the free energy of activation as a function of a reaction coordinate (RC). Models for transition states of catalytic reactions should focus on determining $G^{\ddagger,0}$ and κ .

If barriers are low enough and/or temperatures are high enough, dynamics calculations can be directly used to simulate a reaction in real time and thereby focus on kinetic, thermodynamic, and mechanistic issues. However, this is not feasible if the reaction of interest has a high barrier compared to $k_B T$, where k_B is Boltzmann's constant and T is temperature, unless one employs infrequent event sampling and/or a constraint on the reaction coordinate. In such a case, one can show that it is still possible to obtain statistical information about a given reaction along a reaction coordinate by using umbrella sampling or by enforcing a constrained reaction coordinate and employing generalized normal mode analysis, thermodynamic integration, or free energy perturbation theory where the incremental change in the reaction coordinate is the perturbation (1-3,14-28). In this approach, one selects (or "distinguishes") a specific RC that most conveniently leads the system through an area of interest, for instance the transition state region. The chemical system is then led slowly along the RC, thereby mapping out the regions adjacent to the RC. This slow mapping yields two types of information. First, the dynamical scanning process can escape from local catchment basins and find reaction pathways unforeseen by the operator (29,30). This is an especially important feature if one is trying to explore as yet uncharted territory. Several recent papers show that this approach works very well for finding lowest-energy pathways in catalytic systems like the Ziegler-Natta metallocene type homogeneous catalysts (29,30). Second, by umbrella sampling, generalized normal mode analysis, integrating the effective forces along the reaction coordinate, or free energy perturbation theory, one arrives at the free energy of activation profile mentioned below Eq. (1), that is, the free energy of activation (5,9,12,13) required to move the system from one cut through the RC to another or from reactants to a particular point along the RC. This technique is a very efficient tool to calculate activation free energies and enthalpies in molecular dynamics.

In order to accelerate the rate of a chemical reaction the catalyst must find a way to interact with the substrate(s) so that the resulting free energy of activation barrier or reaction friction becomes lower than that of the original process in the gas phase or in solution. There is no universal theory of the origin of catalytic rate acceleration; however, in light of the considerations of the previous paragraph, we

may attempt to classify the effects into energetic, entropic, or frictional/dynamical. Since energetic stabilization takes place in most cases by non-covalent interactions, it is plausible that electrostatic effects and the participation of ionic and polar species are of utmost importance in catalysis. Electrostatics plays a central role in all of chemistry, and catalytic reactions are no exception. Catalysts may produce a strong electrostatic field around a substrate, and an appropriate model should therefore contain the environment of C, including polar or charged groups and solvent. As mentioned above, aqueous solutions are especially complicated since water is a liquid with a large dielectric constant; thus it has quite a strong influence on molecular transformations of polar species or with polar or charged catalysts. In some cases, transition-metal catalysis may be electrostatic in nature, but in most cases it can be attributed to changing overlap between interacting atomic or molecular orbitals; thus, the effect should typically be described in terms of quantum mechanics. There is evidence that electrostatic catalysis is important for a number of pericyclic reactions (31), and we may speculate that potentially similar effects arise for rearrangements in water or other polar solvents where the initial state of the reaction involves less polar species than the transition state. In such cases metal or other small ions stabilize the transition state by electrostatic interactions. However, for some transition-metal ions, orbital interactions may outweigh electrostatics; thus homogeneous catalysis involving these does not necessarily obey the above rule. For heterogeneous catalysis taking place at interfaces, the arrangement and properties of participating atoms or molecules may differ strongly from the bulk; specific interactions take place here. There are at least two systems, crystal surfaces and zeolite pores, where the electrostatic potential changes extremely rapidly, providing a large electrostatic field difference between the gas phase and the bulk. This may vary in the range of 5 to 20 V/nm and strongly polarize reactant bonds which may result in their fission or enhancement of attack by certain reagents (32). It has been postulated that the catalytic effect of zeolites is mainly due to the strong electrostatic field that may emerge within the pores (33), although this is an incomplete explanation, and one must consider the specific Lewis or Brønsted acid sites that may be present. Electrostatic catalysis in zeolites may be attributed to two main effects. One is the stabilization of cations by the large negative molecular electrostatic potential inside zeolite pores. This effect favors, for example, the formation of protonated species, and thus it may result in stabilization of the corresponding transition states. The other effect is related to the high electrostatic field inside pores that polarizes covalent bonds and promotes them for fission and stabilizes ion pairs.

Entropy effects may play an important role for a number of catalytic processes by immobilizing the reacting partners and thus reducing translational, rotational, or, to a lesser extent, vibrational entropy in the transition state. It is an old hypothesis that enzymes should be capable of efficiently catalyzing reactions with unfavorable entropies of activation by acting as "entropy traps;" this means that the binding energy of the enzyme is used to freeze out rotational and translational degrees of freedom by converting them to confined vibrations in the process of forming the activated complex. These effects may be smaller than previously thought since enzyme molecules are quite flexible, e.g., an examination of the entropic contribution to the rate acceleration of serine proteases indicate that this is a small effect (1).

Frictional effects are usually assumed to be less important than equilibrium free energy effects, but are not always negligible (5,34). As discussed elsewhere (35), "friction" and "nonequilibrium solvation" provide two different ways of looking at the effects that decrease the transmission factor. Nonequilibrium solvation may play a significant role in determining the temperature dependence of reaction rates.

Many catalytic processes involve general acid or base catalysis which can provide an alternative reaction path with lower energetic barriers and different free