

SOLVENT EFFECTS AND CHEMICAL REACTIVITY

Understanding Chemical Reactivity

Volume 17

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Solvent Effects and Chemical Reactivity

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PREFACE

This book gathers original contributions from a selected group of distinguished researchers that are actively working in the theory and practical applications of solvent effects and chemical reactions.

The importance of getting a good understanding of surrounding media effects on chemical reacting system is difficult to overestimate. Applications go from condensed phase chemistry, biochemical reactions *in vitro* to biological systems *in vivo*. Catalysis is a phenomenon produced by a particular system interacting with the reacting subsystem. The result may be an increment of the chemical rate or sometimes a decreased one. At the bottom, catalytic sources can be characterized as a special kind of surrounding medium effect. The materials involving in catalysis may range from inorganic components as in zeolites, homogenous components, enzymes, catalytic antibodies, and ceramic materials.

With the enormous progress achieved by computing technology, an increasing number of models and phenomenological approaches are being used to describe the effects of a given surrounding medium on the electronic properties of selected subsystem. A number of quantum chemical methods and programs, currently applied to calculate in vacuum systems, have been supplemented with a variety of model representations. With the increasing number of methodologies applied to this important field, it is becoming more and more difficult for non-specialist to cope with theoretical developments and extended applications. For this and other reasons, it is deemed timely to produce a book where methodology and applications were analyzed and reviewed by leading experts in the field.

The scope of this book goes beyond the proper field of solvent effects on chemical reactions. It actually goes deeper in the analysis of solvent effects as such and of chemical reactions. It also addresses the problem of mimicking chemical reactions in condensed phases and bioenvironments. The authors have gone through the problems raised by the limitations found in the theoretical representations. In order to understand, it is not sufficient to have agreement with experiments, the schemes should meet the requirements put forward by well founded physical theories.

The book is structured about well defined themes. First stands the most methodologic contributions: continuum approach to the surrounding media (Chapter 1), density

functional theory within the reaction field approach (Chapter 2), Monte Carlo representations of solvent effects (Chapter 3), molecular dynamics simulation of surrounding medium within the *ab initio* density functional framework (Chapter 4). Dynamical aspects of chemical reactions and solvent effects occupies the central focus in Chapters 5 and 6. The last chapter contains a general quantum mechanical analysis of dynamical solvent effects and chemical reactions.

In chapter 1, Profs. Cramer and Truhlar provide an overview of the current status of continuum models of solvation. They examine available continuum models and computational techniques implementing such models for both electrostatic and non-electrostatic components of the free energy of solvation. They then consider a number of case studies with particular focus on the prediction of heterocyclic tautomeric equilibria. In the discussion of the latter they focus attention on the subtleties of actual chemical systems and some of the danger in applying continuum models uncritically. They hope the reader will emerge with a balanced appreciation of the power and limitations of these methods. In the last section they offer a brief overview of methods to extend continuum solvation modeling to account for dynamic effects in spectroscopy and kinetics. Their conclusion is that there has been tremendous progress in the development and practical implementation of useful continuum models in the last five years. These techniques are now poised to allow quantum chemistry to have the same revolutionary impact on condensed-phase chemistry as the last 25 years have witnessed for gas-phase chemistry.

In chapter 2, Profs. Contreras, Pérez and Aizman present the density functional (DF) theory in the framework of the reaction field (RF) approach to solvent effects. In spite of the fact that the electrostatic potentials for cations and anions display quite a different functional dependence with the radial variable, they show that it is possible in both cases to build up an unified procedure consistent with the Born model of ion solvation. The proposed procedure avoids the introduction of arbitrary ionic radii in the calculation of insertion energy. Especially interesting is the introduction of local indices in the solvation energy expression. the effect of the polarizable medium is directly expressed in terms of the natural reactivity indices of DF theory. The paper provides the theoretical basis for the treatment of chemical reactivity in solution.

In chapter 3, Profs. A. González-Lafont, Lluch and Bertrán present an overview of Monte Carlo simulations for chemical reactions in solution. First of all, the authors briefly review the main aspects of the Monte Carlo methodology when it is applied to the treatment of liquid state and solution. Special attention is paid to the calculations of the free energy differences and potential energy through pair potentials and many-body corrections. The applications of this methodology to different chemical reactions in solution are

checked.

In chapter 4, Profs. Corongiu, Estrin, Paglieri and Inquimae consider those systems they have analysed in the last few years, while indicating shortcomings and advantages in different approaches. In the methodological section they pay especial attention to the density functional theory implementation in their computer programs. Especially interesting is the presentation of DF theory and Molecular Dynamics method developed by Carr and Parrinello. Here, the electronic parameters as well as the nuclear coordinates are treated as dynamical variables.

In chapter 5, Prof Hynes reviews the Grote-Hynes (GH) approach to reaction rate constants in solution, together with simple models that give a deeper perspective on the reaction dynamics and various aspects of the generalized frictional influence on the rates. Both classical particle charge transfer and quantum particle charge transfer reactions are examined. The fact that the theory has always been found to agree with molecular dynamics computer simulations results for realistic models of many and varied reaction types gives confidence that it may be used to analyze real experimental results. Another interesting result in MD simulations of S_N2 reaction in solution is that a major portion of the solvent reorganization to a state appropriate to solvating the symmetric charge distribution of the reagents at the barrier top takes place well before the reagent charge distribution begins to change. This shows very clearly for the S_N2 system that one cannot picture the progress of a chemical reaction as a calm progression along the potential of mean force curve (a chemical reaction is intrinsically a dynamic, and not an equilibrium event).

In chapter 6, Profs. Bianco and Hynes give some highlights of a theory which combines the familiar multistate valence bond (VB) picture of a molecular system with a dielectric continuum model for the solvent and includes a quantum model for the electronic solvent polarization. The different weights of the diabatic states going from gas phase to solution introduce easily the polarization of the solute by the reaction field. Non equilibrium effects are introduced dividing the solvent polarization in two components: the electronic polarization (fast) and the reorientation polarization (slow). In this way the theory is capable of describing both the regimes of equilibrium and non-equilibrium solvation. For the latter the authors have developed a framework of natural solvent coordinates. The non-equilibrium free energy surface obtained can be used to analyze reaction paths and to calculate reaction rates constants. Finally, the quantum model for the electronic solvent polarization allows to define two limits : self consistent (SC) and Born-Oppenheimer (BO). In the SC case, the electronic solvent frequency is much smaller than the frequency of interconversion of VB states. So, the solvent sees the average charge distribution. In the BO case, it happens the contrary. Now the electronic solvent frequency is much faster than VB

interconversions. It means the solvation of localized states and, as a consequence, that the free energy from the solvent point of view is lower than the solvation of the delocalized self-consistent charge distribution.

In chapter 7, Profs. Tapia, Andrés and Stamato give an extended analysis of the quantum mechanics of solvent effects, chemical reactions and their reciprocal effects. The stand point is somewhat different from current pragmatic views. The quantum mechanics of n -electrons and m -nuclei is examined with special emphasis on possible shortcomings of the Born-Oppenheimer framework when it is applied to a chemical interconversion process. Time dependent phenomena is highlighted. The authors go a step beyond previous wave mechanical treatments of solvent effects by explicitly including a time-dependent approach to solvent dynamics and solute-solvent coupling. Solvent fluctuation effects on the solute reactive properties include now most of the 1-dimensional models currently available in the literature. Time dependent effects are also introduced in the discussion of the quantum mechanics of chemical interconversions. This perspective leads to a more general theory of chemical reactions incorporating the concept of quantum resonances at the interconversion step. The theory of solvent effects on chemical reactions is then framed independently of current quantum chemical procedures. As the chapter unfolds, an extended overview is included of important work reported on solvent effects and chemical reaction.

A book on solvent effects today cannot claim completeness. The field is growing at a dazzling pace. Conspicuous by its absence is the integral equation description of correlation functions and, in particular, interaction-site model-RISM- by D. Chandler and H.C. Andersen and later extended for the treatment of polar and ionic systems by Rossky and coworkers. Path integral method is currently being employed in this field. By and large, we believe that the most important aspects of the theory and practice of solvent effects have been covered in this book and we apologize to those authors that may feel their work to have been inappropriately recognized.

Finally, the editors of this book would tend to agree with Cramer and Truhlar's statement that contemporary advances in the field of solvent effect representation would allow quantum chemistry to have the same revolutionary impact on condensed-phase chemistry as the last 25 years have witnessed for gas-phase chemistry. We hope this book will contribute to this end.