

**Sulfur-Centered Reactive
Intermediates in
Chemistry and Biology**

Sulfur-Centered Reactive Intermediates in Chemistry and Biology

Edited by

Chryssostomos Chatgililoglu

Consiglio Nazionale delle Ricerche
Ozzano Emilia (Bologna), Italy

and

Klaus-Dieter Asmus

Hahn-Meitner-Institut
Berlin, Federal Republic of Germany

Plenum Press

New York and London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of a NATO Advanced Study Institute on
Sulfur-Centered Reactive Intermediates in Chemistry and Biology,
held June 18-30, 1989,
in Maratea, Italy

Library of Congress Cataloging-in-Publication Data

NATO Advanced Study Institute on Sulfur-Centered Reactive
Intermediates in Chemistry and Biology (1989 : Maratea, Italy)
Sulfur-centered reactive intermediates in chemistry and biology
edited by Chrysostomos Chatgililoglu and Klaus-Dieter Asmus.
p. cm. -- (NATO ASI series. Series A, Life sciences : v.
197)
"Proceedings of a NATO Advanced Study Institute on Sulfur-Centered
Reactive Intermediates in Chemistry and Biology, held June 18-30,
1989, in Maratea, Italy"--Verso t.p.
"Published in cooperation with NATO Scientific Affairs Division."
Includes bibliographical references and index.
ISBN 0-306-43723-6
1. Organosulphur compounds--Congresses. I. Chatgililoglu,
Chrysostomos. II. Asmus, Klaus-Dieter. III. North Atlantic Treaty
Organization. Scientific Affairs Division. IV. Title. V. Series.
QD412.S1N37 1989
547'.06--dc20 90-14295
CIP

© 1990 Plenum Press, New York
A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted
in any form or by any means, electronic, mechanical, photocopying, microfilming,
recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

FOREWORD

A wonderfully successful NATO Advanced Study Institute on "Sulfur-Centered Reactive Intermediates in Chemistry and Biology" was held 18-30 June, 1989, at the Hotel Villa del Mare in Maratea, Italy. Despite the beautiful setting with mountains behind us and overlooking the clear blue Mediterranean Sea under a cloudless sky (and with a private beach available), the lectures were extremely well attended. While some credit can go to the seriousness of the students, more must go to the calibre of speakers and the high quality of their presentations. The Director, Dr. C. Chatgililoglu, and Co-Director, Professor K.-D. Asmus, are to be congratulated for putting together such an outstanding scientific program. Dr. Chatgililoglu is also to be commended for arranging an equally stimulating social program which included bus, train and boat trips to many local sites of interest.

It was particularly fitting that a meeting on the chemistry and biochemistry of sulfur should be held in Italy since Italian chemists have made major contributions to our understanding of the organic chemistry of sulfur, including the chemistry of its reactive intermediates. The early Italian interest in sulfur chemistry arose from the fact that Italy, or more specifically, Sicily, was a major world producer of sulfur prior to the development and exploitation of the Frasch process in Texas and Louisiana. More recently, under stimulating guidance of the late, great Italian chemist, Professor Angelo Mangini of Bologna, studies on the organic chemistry of sulfur and, particularly, on sulfur-centered reactive intermediates have received new impetus and have flourished in Italy. Several of Professor Mangini's scientific "children" attended the meeting and so did some of their scientific children (Mangini's "grandchildren"). I know that he would have approved of this meeting and believe that he was with us in spirit throughout the two weeks.

The speakers and the students were mainly chemists. However, their scientific backgrounds and research interests varied enormously - theoretical chemistry, gas phase kinetics, thermodynamics and so on, all the way to the mechanisms of enzyme catalyzed reactions. This interdisciplinary approach, which covered the entire field of sulfur chemistry, is a credit to the organizers of the meeting and their judgement in choosing speakers. Certainly, it made the meeting especially valuable to all attendees. After each talk, one had learned something new, interesting and, quite frequently, of direct relevance to one's own research program. Because of the interdisciplinary nature of the meeting audience participation was exceptionally strong. Long and vigorous discussion followed each presentation and, indeed, often continued long into the night!

For all scientists interested in the chemistry and biochemistry of sulfur this book provides a valuable and permanent record of NATO's 1989 ASI on sulfur. Please read and enjoy the 39 papers presented by 26 scientists from 7 NATO countries and Japan.

5 July 1989

K. U. Ingold
Ottawa, Canada

PREFACE

This book contains the main lectures given at the NATO Advanced Studies Institute on "Sulfur-Centered Reactive Intermediates in Chemistry and Biology" held in Acquafredda di Maratea (Italy) June 18-30, 1989. The first chapters consider theoretical aspects and give a survey of general thermodynamic properties of sulfur functionalities in molecules. A second larger group of articles covers the variety of experimental techniques which have most successfully been applied for the investigation of sulfur-centered reactive intermediates. The generation and the properties of these species, particularly radical and non-radical cations, are extensively described in the following papers. Many interesting and important studies in this field could not have been performed without especially tailored molecules. Consequently, their synthesis is a subject covered in this book. Equally interesting will be the other synthesis papers describing the application of sulfur-organic compounds and sulfur-centered radicals for the preparation of new compounds and the understanding of reaction mechanisms. The final, large section highlights the role of the sulfur compounds and sulfur-centered radical species in biochemistry and biology. The reader will realize how many of the interpretations and conclusions in this "life science" oriented subject have benefited from the fundamental knowledge described in the first part of the book.

While we could not cover all possible topics in the still expanding subject of sulfur-centered reactive intermediates, an effort has been made to provide the state-of-the-art on, at least, some key aspects in this field. We believe this book will be useful for the scientific community as a reference work as well as an introduction to the various fields presented in the individual chapters by authors who are top experts in their respective disciplines.

The meeting received a great impetus from the fact that scientists got together who would not necessarily attend the same conferences, but could now discover the full value of broad and interdisciplinary discussions. This, and also common interests in the many cultural and social activities offered by our Italian hosts (including the appreciation of surprising talents of young as well as established scientists in the game of football/soccer), were the basis for the high spirit of this, as we feel, most successful summer school.

Our special thanks are due to NATO, Consiglio Nazionale delle Ricerche, Progetto Finalizzato "Chimica Fine II", Università di Basilicata, Hahn-Meitner-Institut Berlin, Regione di Basilicata, Azienda Autonoma Soggiorno e Turismo di Maratea, Glaxo S.p.A. and Farmitalia Carlo Erba who kindly provided the financial support.

Finally, a word on the preparation of this book. Despite all the work which had to be invested into collecting, reading, editing, typing, and correcting the contributions, it has been an interesting and scientifically rewarding task. If completion took a bit longer than originally anticipated our only excuse is that we, a small editing crew, (and all official guide-and deadlines) totally underestimated the real amount of work coming up. Fortunately we could count on the professional and always interested help of Mrs. Kim Kube for the typing and Dr. Wolfgang Hoyer for the computer drawn chemical structures. They and all those who in one way or the other contributed to the finishing of this book deserve our sincere thanks.

K.-D. Asmus
Berlin, F. R. Germany

C. Chatgililoglu
Bologna, Italy

CONTENTS

Force-Field and Molecular Orbital Calculations in Organosulfur Chemistry	1
<i>T. Clark</i>	
Electronic Transitions in Sulfur-Centered Radicals by Means of MSX α Calculations . . .	7
<i>M. Guerra</i>	
The Electronic Properties of Sulfur-Containing Substituents and Molecules: An Ab Initio Study	13
<i>T. Clark</i>	
Reactivity of Sulfur-Centered Nucleophiles Towards Dia- and Paramagnetic Reagents. The Frontier Orbitals Approach	19
<i>M. Arbelot, A. Samat, M. Rajzmann, M. Meyer, A. Gastaud, and M. Chanon</i>	
Alkanethiylperoxyl Radicals	31
<i>C. Chatgililoglu and M. Guerra</i>	
Thermochemistry of Sulfur-Centered Intermediates	37
<i>D. Griller, J. A. Martinho Simões, and D. D. M. Wayner</i>	
Experimental Procedures in Electrolysis	53
<i>H. Lund</i>	
Single Electron Transfer in Aliphatic Nucleophilic Substitution	69
<i>H. Lund</i>	
Photochemistry as a Tool for the Study of Reactive Intermediates	83
<i>G. S. Wilson</i>	
Electrochemical Reduction of Some Sulfur Compounds	93
<i>H. Lund</i>	
Photocatalytic Formation of Sulfur-Centered Radicals by One-Electron Redox Processes on Semiconductor Surfaces	103
<i>D. Bahnemann</i>	
Applications of Pulse Radiolysis for the Study of Short-Lived Sulphur Species	121
<i>D. A. Armstrong</i>	
Structure and Reaction Mechanisms in Sulphur-Radical Chemistry Revealed by E.S.R. Spectroscopy	135
<i>B. C. Gilbert</i>	

Sulfur-Centered Three-Electron Bonded Radical Species	155
<i>K.-D. Asmus</i>	
Radical Cations of Conjugated Cyclic Disulfides	173
<i>G. A. Russell and W. C. Law</i>	
Beam Experiments as a Means for the Generation of Elusive Sulfur-Containing Molecules	185
<i>D. Sülzle, T. Drewello, and H. Schwarz</i>	
Dications from Cyclic Polythioethers	193
<i>H. Fujihara and N. Furukawa</i>	
Sulfenylium Cation Carriers in Chemistry and Biochemistry	197
<i>G. Modena and L. Pasquato</i>	
Neighboring Group Participation: General Principles and Application to Sulfur-Centered Reactive Species	213
<i>R. S. Glass</i>	
Design, Synthesis, and Conformational Analysis of Compounds Tailored for the Study of Sulfur-Centered Reactive Intermediates	227
<i>R. S. Glass</i>	
The Stereochemical Course of Sulphate Activation and Transfer	235
<i>G. Lowe</i>	
Anionic Organosulfur Compounds in Synthesis: New Applications of the Ramberg-Bäcklund Reaction	251
<i>E. Block, D. Putman, and A. Schwan</i>	
The Synthesis and Metal Complexes of Sulfur-Containing Models for Nitrogenase Enzymes	269
<i>E. Block, M. Gernon, and J. Zubieta</i>	
Biologically Active Organosulfur Compounds from Garlic and Onions: The Search for New Drugs	285
<i>E. Block</i>	
Free Radical Processes in the Reactions of Organometallics with Organic Sulfur Compounds	291
<i>G. A. Russell and P. Ngoviwatchai</i>	
The Invention of Radical Chain Reactions of Value in Organic Synthesis	303
<i>F. Minisci</i>	
Recent Advances in the Chemistry of Compounds Containing S-Si Moieties	319
<i>M. Ballestri, C. Chatgililoglu, P. Dembeck, A. Guerrini, and G. Seconi</i>	
Reaction Kinetics of Sulfur-Centered Radicals	327
<i>D. Griller and J. A. Martinho Simões</i>	
Redox Systems with Sulphur-Centered Species	341
<i>D. A. Armstrong</i>	

Electrochemistry of Thioethers as Models for Biological Electron Transfer	353
<i>G. S. Wilson</i>	
Free-Radical Reactions Involving Thiols and Disulphides	359
<i>C. v. Sonntag</i>	
Hydrogen Abstraction by Thiyl Radicals from Activated C-H Bonds of Alcohols, Ethers and Polyunsaturated Fatty Acids	367
<i>C. Schöneich, M. Bonifačić, U. Dillinger, and K.-D. Asmus</i>	
Thiyl Free Radicals: Electron Transfer, Addition or Hydrogen Abstraction Reactions in Chemistry and Biology, and the Catalytic Role of Sulphur Compounds	377
<i>C. Dunster and R. L. Willson</i>	
Free Radical Transfer Involving Sulphur Peptide Functions	389
<i>W. A. Prütz</i>	
Electron Spin Resonance Investigation of the Thiyl Free Radical Metabolites of Cysteine, Glutathione, and Drugs	401
<i>R. P. Mason and D. N. Ramakrishna Rao</i>	
Sulphur Compounds and "Chemical Repair" in Radiation Biology	409
<i>C. v. Sonntag and H.-P. Schuchmann</i>	
Thiol Reactivity Towards Drugs and Radicals: Some Implications in the Radiotherapy and Chemotherapy of Cancer	415
<i>P. Wardman</i>	
Vivo Hemoglobin Thiyl Radical Formation as a Consequence of Hydrazine-Based Drug Metabolism	429
<i>R. P. Mason and K. R. Maples</i>	
The Biological Actions of the Glutathione/Disulfide System: An Overview	435
<i>M. Quintiliani</i>	
EX	445

FORCE-FIELD AND MOLECULAR ORBITAL CALCULATIONS IN ORGANOSULFUR CHEMISTRY

Timothy Clark

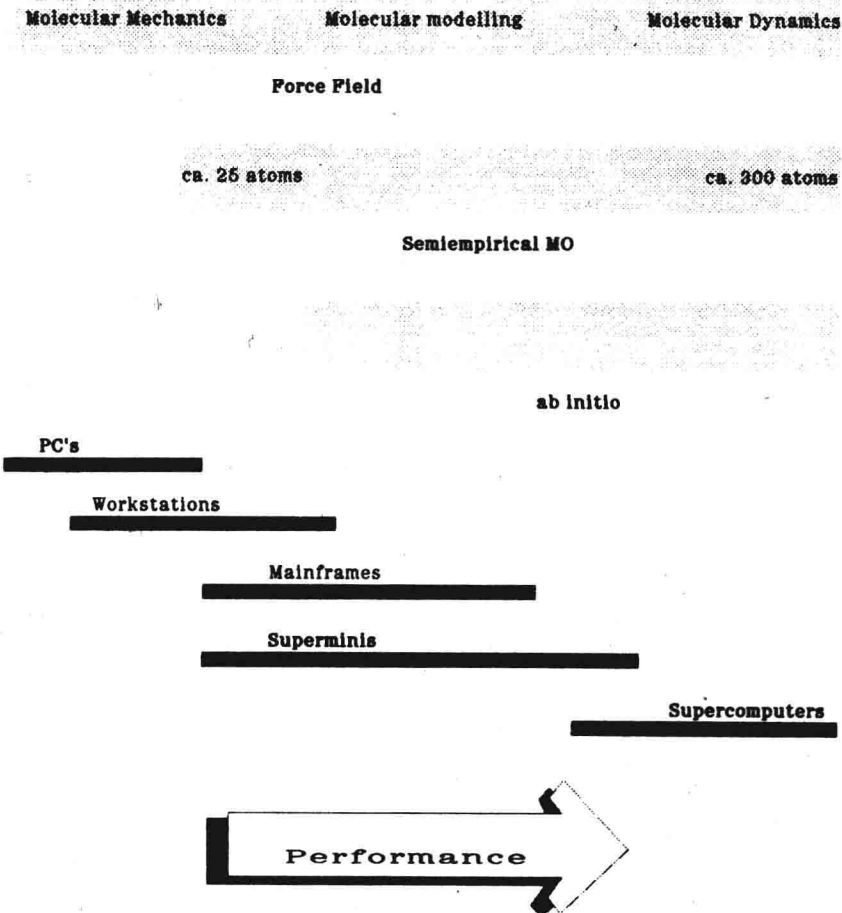
Institut für Organische Chemie der
Friedrich-Alexander-Universität Erlangen-Nürnberg
Henkestraße 42, 8520 Erlangen, Fed. Rep. Germany

Chemical structure and energy calculations¹ are unique among the available research tools in that they do not require the molecule in question to have been made or isolated - or even that it is capable of existence. Calculations are capable of delivering structures, energies and electronic properties such as dipole moments, charge distributions or ionization potentials with reasonable accuracy at a fraction of the cost (both financial and in time and effort) of comparable experimental studies. Two main types of structure and energy calculation are available: force-field (molecular-mechanics) and molecular orbital (MO) calculations. The latter can be subdivided into the semiempirical (MINDO/3, MNDO, AM1, PM3 etc.) and *ab initio* techniques. The object of this article is to provide an overview of the cost (in computer time), applicability and accuracy of the various methods.

COMPUTER REQUIREMENTS

Computer requirements for the different methods differ enormously. Simple molecular mechanics optimizations on reasonably sized molecules can be done easily on a PC. However, large molecular dynamics simulations, which use the same basic model as molecular mechanics, may require a supercomputer. Semiempirical MO calculations can be done on PC's for small molecules, but require a workstation or supermini for large (ca. 150 atom) molecules. *Ab initio* can be performed very effectively on the better workstations, but may require supermini or supercomputer performance for very large or very high level calculations. Scheme 1 provides a rough overview of the situation.

Reference 1 gives a table (p. 3) of the computer times needed to optimize the geometry of propane using the various theoretical techniques.¹ These vary from 0.8 seconds for molecular mechanics to almost 5,000 seconds for an *ab initio* 3-31G* calculation. This is by no means the highest practicable *ab initio* calculation for a molecule of this size, so that a factor of 10,000 between computer time requirements for molecular mechanics and high level *ab initio* is not unreasonable. As a rough guideline, the computer time ratio *force-field* : *semiempirical MO* : *ab initio* is about 1 : 10 - 100 : 500 - 10,000. The last number could equally well be infinity because the level at which *ab initio* calculations can be performed is open-ended. These large differences mean that an understanding of the characteristics of each method is essential for the effective use of computer facilities.



Scheme 1. A schematic view of the suitability of different types of computer (dark lines) to different chemical applications (grey boxes).

FORCE-FIELD METHODS

Force-field, or molecular mechanics, methods^{1,2} are based on a simple mechanical model of molecules. Bonds between atoms are considered to behave like springs that obey a modified version of Hooke's law. Similarly, bond angles have preferred values from which they can be deformed according to a potential that depends on the square of the deformation plus higher terms. Torsional potentials (1-, 2- and 3-fold) are used for each pair of vicinal bonds and compound terms that depend both on the bond lengths to a given atom and to the angles between the two bonds (stretch-bend terms) are also used. Steric interactions are taken into account by considering van der Waals interactions between individual atoms. Van der Waals interactions between geminal atoms are not usually considered because they are accounted for by the angle-bending and stretch-bend terms. The sum of these potentials is known as the force-field. Force-fields are parametrized by varying the preferred lengths and angles and the force constants governing the individual potentials until as good a fit as possible to experimental values (usually heats of formation and geometries) is obtained. Because there are any number of different force-fields that can give a good fit to a given set of experimental data, the individual energies (stretching, torsional, van der Waals etc.) do not have any physical meaning and should not be used to interpret experimental findings.

Because force-field methods are parametrized to fit experiment, the quality of the results depends heavily on the quality and quantity of the parametrization data-set. Thus, the most accurate force-fields are available for the alkanes, for which a large body of experimental data exists. Molecular mechanics for alkane heats of formation and structures can be of experimental quality or better. Structural elements for which less data are available, such as sulfur-containing groups, do not give results of such high accuracy, but are nevertheless well treated. The two great weaknesses of force-field calculations are their inability to deal with unusual electronic effects, which are not included in the theoretical model, and the fact that they are limited to stable equilibrium geometries because the parametrization data-sets can only include such species. Clearly, they cannot deal with reactions in which bonds are made and broken without an extra parametrization for this process, but they may also give poor results for the activation energies of processes such as conformational interconversions, in which no bonds are made or broken.

Force-field programs for simple molecular mechanics optimizations range from Allinger's MM287 (available from the Quantum Chemistry Program Exchange, QCPE) to the commercially available "molecular modelling" packages that provide color graphic input and output facilities. Care should be taken with such packages that the force-field being used really is what it is supposed to be. This can be checked by comparing results for some test molecules with the original literature.

SEMIEMPIRICAL MOLECULAR ORBITAL METHODS

Although there are many different semiempirical MO-methods, the best known and most widely used are those developed by Michael Dewar and his school. MINDO/3, the first such method to gain general acceptance, is now outdated and has been replaced by MNDO,³ AM1⁴ and PM3.⁵ These are all NDDO-based methods and the latter two (which differ only in the parameter sets used) were developed to eliminate some of the known weaknesses of MNDO. Two programs that incorporate these methods, MOPAC and AMPAC, are available from QCPE. Vectorized versions that provide very high performance on superminis and supercomputers are available for some machines. Scheme 2 shows the elements for which MNDO, AM1 and PM3 have been parametrized.

There are several important points to consider when calculating sulfur compounds – especially with MNDO. The first is that there are two sets of MNDO parameters for sulfur and silicon. The original parametrizations for these elements were not as successful as had been hoped and were later repeated and new parameter sets introduced. Care should be taken when using older programs that the correct parameter set is installed. MNDO-calculations should not be used for sulfones and sulfoxides or other "hypervalent" sulfur compounds, for which they give very large errors. This was originally thought to be due to the fact that MNDO uses only *s*- and *p*-orbitals and that *d*-orbitals are necessary in order to describe sulfones and sulfoxides correctly. However, Stewart included hypervalent compounds in the parametrization set for PM3 and was able to obtain satisfactory results for sulfones and sulfoxides. Dewar's AM1-parameters for sulfur are also able to treat sulfones and sulfoxides adequately.

Care should be taken when using MNDO because it does not reproduce hydrogen bonds. For applications where this is important, AM1 or PM3 should be used. These two methods are comparable in performance, although PM3 is probably more widely applicable and AM1 has the edge if rotation barriers in conjugated systems, such as peptides, are important.

Generally, semiempirical MO-methods offer a good compromise between efficiency and accuracy for questions that cannot be answered by force-field calculations. This includes all problems in which electronic effects are important as well as reactivity problems. Molecular mechanics is probably more useful if purely conformational problems are of interest.

MNDO-Parameters

H						
Li	Be	B	C	N	O	F
	Mg	Al	Si	P	S	Cl
	Zn		Ge			Br
	Hg		Sn			I
			Pb			

AM1-Parameters:

H						
	B	C	N	O	F	
	Al	Si	P	S	Cl	
	Zn		Ge			Br
	Hg					I

PM3-Parameters:

H						
		C	N	O	F	
		Si	P	S	Cl	
						Br
						I

Scheme 2. Elements for which MNDO, AM1 and PM3 parameters are available (Nov. 1989). Lithium and magnesium were parametrized for MNDO by groups other than that of Prof. Dewar.

Semiempirical calculations can now be done for many experimental compounds and are being used for increasingly larger systems, such as enzyme models, as computer hardware becomes more sophisticated. A RISC-workstation dedicated to semiempirical calculations is a very powerful research tool indeed.

AB INITIO CALCULATIONS

Ab initio molecular orbital theory⁶ is the most computationally demanding of the three techniques covered here. That does not always mean that it is the most accurate. *Ab initio* calculations that are too large to allow the use of a reasonable basis set or that cannot be fully optimized are likely to be less reliable than (far cheaper) AM1 or PM3 calculations on the same system. If, however, the molecules being studied are small enough for a full *ab initio* investigation at an adequate level of theory, the best results can almost always be expected from the *ab initio* calculations.

One major difference between *ab initio* and semiempirical techniques is that the level at which the calculation is performed can be varied using *ab initio* theory. There are two major ways to vary the level of the calculation *via* the basis set and the level at which electron correlation is treated. The smallest basis sets (the atomic orbitals that are combined to give the molecular orbitals) are known as minimal bases because they contain only enough orbitals per atom to accommodate the electrons of the neutral atom and to maintain spherical symmetry. Thus, a minimal basis for carbon consists of $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals, and for hydrogen only $1s$. STO-3G is probably the best known minimal basis set. The acronym means Slater Type Orbitals simulated by 3 Gaussian functions. Gaussian functions are used rather than Slater orbitals because integrals between Gaussian functions are easier to calculate than those between Slater functions. Minimal basis sets are, however, poorly suited for sulfur calculations. Split-valence bases are more sophisticated. Their valence orbitals are split into compact (inner) and diffuse (outer) components. Linear combinations of inner and outer components give a range of orbital size in the MO's and thus provide more flexibility than a minimal basis. The most widely used split-valence basis is probably 3-21G (3 Gaussians for the core orbitals, 2 for the inner and 1 for the outer valence orbitals), which was developed for fast geometry optimizations. A variation of 3-21G is 3-21G(*) (sometimes written as 3-21G*), which has an extra set of d -functions for second row elements. A more satisfactory, although more expensive, solution is to use d -functions on all non-hydrogen atoms in a polarization basis set such as 6-31G*. In most molecules, the role of the d -functions is to polarize the p -orbitals, rather than to act as valence orbitals. This effect is, however, very important. Geometry optimizations at 6-31G* reliably predict structures and relative energies of sulfur compounds.

Normally, geometry optimizations are performed at the self-consistent field (SCF), or Hartree-Fock (HF) level. In this approximation, the electron-electron repulsion is calculated by considering the repulsion between a given electron and the mean field of all the others. Because, however, the individual electrons tend to avoid each other, this mean field approximation calculates a repulsion energy that is too high. Additional corrections must be applied to take the correlated motions of the electrons into account. This electron correlation is often not important for geometry optimizations, which are usually carried out at the SCF-level, but has important energetic consequences. Therefore, energy calculations are often done on the SCF-geometries with some sort of correlation correction. This may be by means of configuration interaction (CI), in which many electronic configurations are allowed to mix, or by perturbation theory. The best known perturbational techniques are the Møller-Plesset methods. Møller-Plesset corrections can be calculated to second, third or fourth order (MP2, MP3 and MP4, respectively). Fourth order corrections may include only single and double excitations (MP4sd), singles, doubles and quadruples (MP4sdq) or singles, doubles, triples and quadruples (MP4sdtq). Although energies are usually quoted at the last level, MP4sdq is the default level for the Gaussian programs, so that the exact MP4-level of a given calculation should be checked carefully. Hehre, Radom, Schleyer and Pople⁶ give a useful overview of *ab initio* techniques.

Ab initio programs are more complex than their semiempirical counterparts, and therefore often more expensive. The best known are the Gaussian series of programs from Gaussian Inc. The most recent version is Gaussian 88, but Gaussian 86 is still the most modern version available for some types of machines. A very useful (and much cheaper) alternative to the Gaussian programs is Monstergauss from the University of Toronto. Although not as versatile as Gaussian 88, Monstergauss is far less machine-dependent and can easily be adapted to most computers. For vector computers (superminis and supercomputers), Cadpac is usually much faster than Gaussian 88, especially for MP2 optimizations and frequency-calculations and for molecules of high symmetry. Cadpac is available from the University of Cambridge. Older *ab initio* programs, such as HONDO or Gamess, are still in use for specialized applications.

SUMMARY

The three types of calculations described here provide a wide range of useful applications in sulfur chemistry. Force-field methods are cheap and well suited to conformational problems or those in which the relative stabilities of a series of stable molecules are of interest. Semiempirical MO-calculations are less accurate but far more flexible and can now be applied routinely to experimentally accessible molecules including sulfoxides and sulfones. *Ab initio* calculations at adequate levels are well suited to accurate studies on small molecules and for basic research into the electron properties of sulfur-containing moieties.

REFERENCES

1. T. Clark, "A Handbook of Computational Chemistry", Wiley, New York (1985).
2. U Burkert and N.L. Allinger, "Molecular Mechanics", ACS Monograph 177, American Chemical Society, Washington, DC (1982).
3. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.* 99:4899, 4907 (1977).
4. M.J.S. Dewar, E.G. Zebisch, E.F. Healy, and J.J.P. Stewart, *J. Am. Chem. Soc.* 107:3902 (1985).
5. J.J.P. Stewart, *J. Comput. Chem.* 10:209, 221 (1989).
6. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, "Ab Initio Molecular Orbital Theory", Wiley, New York (1986).

ELECTRONIC TRANSITIONS IN SULFUR-CENTERED RADICALS BY MEANS OF MSX α CALCULATIONS

Maurizio Guerra

I. Co. C. E. A.
Consiglio Nazionale delle Ricerche
40064 Ozzano Emilia (Bologna), Italy

Highly reactive sulfur-centered radicals, which play an important role in air pollution and in biological systems, are usually identified by their UV/visible absorption and/or ESR spectra. Spectral information are sometimes insufficient for an unequivocal characterization of the transient species. Their identification could be achieved by comparing the optical absorption spectra with the energy and intensity of electronic transitions computed using quantum mechanical methods. The MSX α method¹ has proved to be a powerful tool for assigning optical transitions in radicals,² and is used to assign the spectral bands of transient sulfur-centered radical species to specific electronic transitions.³

CALCULATIONS OF THE ELECTRONIC TRANSITIONS IN RADICALS BY MEANS OF THE MSX α METHOD

The MSX α Method

The MSX α method is a "first principle" and basis set independent method based upon an approximate potential. The statistical treatment of the exchange interaction reduces the N-electron Schrödinger equation to a set of one-electron differential equations. (in atomic units)

$$[-1/2 \nabla^2 + V_C(1) + V_{xc}(1)] \Psi(1) = \epsilon \Psi(1) \quad (1)$$

The first two terms represent the kinetic and Coulombic potentials, respectively, and V_{xc} is a local potential which takes into account both of the exchange potential and electron correlation. The simplest and most widely utilized exchange-correlation potential is related to the local electronic charge density, ρ , and a scaling factor α :

$$V_{xc} = -6\alpha [3\rho(r)/8\pi]^{1/3} \quad (2)$$

The multiple scattering procedure allows an effective solution of the mono-electronic equations. The coordinate space of the molecule is partitioned into three regions, as shown for the methyl radical in Figure 1. In the atomic regions (I) which are inside the spheres centered on the atoms and in the extra-molecular region (III), which is outside the outer-sphere surrounding the entire molecule, the potential is assumed to be spherically symmetric and the electronic wavefunction is expanded in real spherical harmonics. In the intersphere

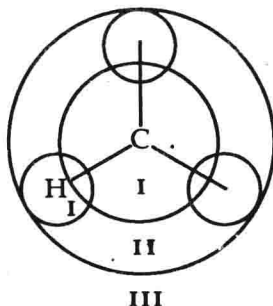


Fig. 1. Division of space in the MX α method into atomic (I), intersphere (II), and extramolecular (III) regions for the methyl radical.

region (II), which is the region between the atomic spheres and the outer-sphere surrounding the entire molecule, the potential is taken to be a constant, determined by the volume average of the potential, and a multicenter expansion of the wavefunction is used. The expansion coefficients are determined by solving a set of homogeneous linear equations under the condition that the wavefunction and its first derivative are continuous at the sphere boundaries.

The Transition State Concept for Computing Electronic Transitions

In the X α theory the orbital eigenvalues ϵ_i are related to the X α statistical total energy, $\langle E_{X\alpha} \rangle$, as the first derivatives of the total energy with respect to the orbital occupation number n_i :

$$\epsilon_i = \partial \langle E_{X\alpha} \rangle / \partial n_i \quad (3)$$

The eigenvalues ϵ_i are then equal to the slope of the total energy function rather than the difference between two values of the total energy as in Hartree-Fock theory (Koopmans' theorem).⁴ Consequently the energy variation occurring in an electronic transition can be obtained by performing calculations on a state (transition state) where the occupation number of the orbitals are halfway between those of the initial and final electronic states.⁵ For an excitation from the i -th to the j -th orbital

$$\Delta E_{i \rightarrow j} = (\epsilon_j - \epsilon_i)_{ts} + \text{third order terms} \quad (4)$$

Efficiency

The MSX α approach has a number of advantages over the more traditional LCAO-SCF method for assigning optical absorption spectra in radicals. The radial flexibility of the wavefunction which can efficiently account for both single center and multicenter charge distribution, allows both the valence and Rydberg states to be treated at the same level of accuracy. Some of the pitfalls of using an atom-centered LCAO expansion for describing Rydberg states are thus avoided. The existence of an excited state depends on the potential and not on the basis set. Imaginary excited states which are computed in LCAO approaches with split-valence basis sets do not occur. The transition state method, used to evaluate the transition energies, takes into account the electron relaxation occurring during the excitation as in the Δ SCF approach. The transition state procedure has, however, two advantages over the more traditional Δ SCF approach. Transition energies are evaluated as the difference of eigenvalues and not as the difference of the total energy of separate calculations. Errors in numerical procedure are thus avoided. The variational collapse of higher excited states on

the lowest excited state of the same symmetry which complicates calculations of the corresponding transition energies does not occur. Obviously the best theoretical tool for assigning the absorption spectra is to perform large scale CI calculations, however, the MSX α method has the advantage of requiring limited computer resources so that large polyatomic systems can be easily investigated. Furthermore, higher atomic number elements can be treated by including scalar relativistic corrections. For example, electronic transition energies were computed for systems as large as triphenyl-silyl-, -germyl and -stannyl radicals. For the latter radical scalar relativistic calculations were performed.⁶

Reliability

The best procedure for computing optical transitions in radicals with the MSX α method was established by performing different types of MSX α calculations on alkyl and H_3M^\bullet ($M = Si, Ge$) radicals. In highly symmetric radicals R_3X^\bullet , vertical transition energies to Rydberg orbitals were reproduced with an accuracy comparable to that obtained with CI calculations employing large basis sets. The deviation from experiment is about 2000 cm^{-1} both for CI and the MSX α method. The valence transitions have not been experimentally determined for these radicals, but the difference between MSX α and CI valence transition energies is less than 1000 cm^{-1} . In asymmetric radicals valence transitions are described with the same accuracy as found with highly symmetric radicals, whereas the Rydberg transitions are described

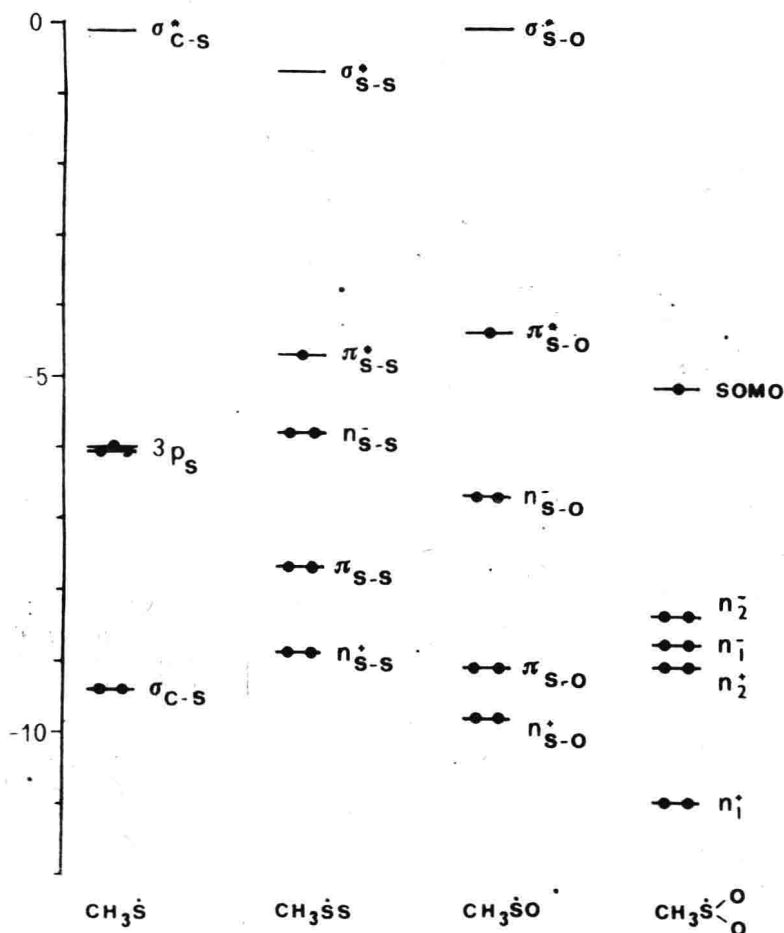


Fig. 2. MSX α eigenvalues, ϵ_i , of the ground state for sulfur-centered radicals.