Chapter 1. Introduction

1.1. An overview of computational chemistry

While atomic physics is concerned with the core electrons in atoms, chemists are primarily interested in understanding the behaviour and interactions between the valence electrons in molecules. Quantum mechanical laws describe the behaviour of electrons and nuclei in atoms. Since it has been demonstrated that quantum mechanics adequately describes the physics governing chemical problems, the application of these laws to chemical phenomena gives rise to the non-experimental field of quantum chemistry.

Quantum chemistry, in principle, deals only with problems where quantum aspects are considered; it is a subfield of a wider non-experimental area of chemistry: modern theoretical chemistry. Theoretical chemistry has been traditionally associated with paper and pencil type of research, and the development of new theories and approximations. In modern research the implementation of new methods in computer programs has led to dramatic advances. Computers are used to test new methods and to investigate interesting chemical problems. The role of computers in the development of theoretical chemistry led to the emergence of the new field of computational chemistry.

Computational chemistry[1] is as wide as everything else in science, and faces challenges in many directions, *e.g.*, reaction mechanisms and dynamics, spectroscopy, condensed-phase studies. Among other things, computer-based research has provided explanations for experimental discoveries, helped calculate parameters not yet measured experimentally and develop chemical theories (*e.g.*, ozone depletion). Furthermore, computational chemistry has aided in our understanding of biochemical processes (*e.g.*, enzymatic reactions, photosynthesis), assisted in the design of new drugs and chemical compounds in general with specific properties, and led to the discovery of structure-property-reactivity relationships.

Chapter 2 will provide a simple account of important and basic features of different methods of computational chemistry that were applied during the development of this thesis.

1.2. On the importance of environmental issues

Annual budgets for environmental research, education and scientific assessment have increased dramatically in recent years. This is clear evidence of the critical importance of environmental issues. Unfortunately, for countries with emerging economies these issues will take much longer to become important priorities.

Environmental research is a complex blend of pursuits that have several objectives, as has been recently pointed out:[2] "To some, the highest form of environmental research is that which seeks only to extend knowledge and is driven by a combination of curiosity and disciplinary traditions. It seeks to describe the structure and function of the natural world, as well as the relationship between this world and humans or human civilizations. (…) Another form of environmental research focuses on the changes that are taking place in the natural and human environments as a result of human activity, either to understand these changes or to seek solutions." Very often, the systems to deal with are extremely complicated and models have to be used to study them. The verification of such models is expensive and usually only approximate measurements and estimates can be made.

Industrial wastes discharged into lakes, rivers and oceans are destroying life in these environments and also indirectly outside them. Industrial emission of toxic gases are affecting agriculture, and provoking health problems,[3] climate changes[4] and the variation of the atmosphere's chemical composition, among other disastrous consequences. In atmospheric chemistry very well known problematic situations have developed such as those associated with photochemical smog, the presence of tropospheric ozone, acid rain, the accumulation of greenhouse gases, the stratospheric ozone-layer depletion, and several others.[5] The development of solutions for these and other problems has become an important environmental challenge.[6]

One hopes there is still time to reverse or counteract the damage provoked by human activity over the many years of economic and industrial development. Definitely this task will require the creative and persistent work of multidisciplinary teams around the world.

The studies compiled in this thesis are computational chemistry applications to subjects of environmental interest. In the first part, reactions that are of interest in atmospheric chemistry are studied from the kinetic point of view. The second part is devoted to the calculation of excited states in a family of compounds whose negative environmental consequences are well known.

1.3. Kinetic calculations in atmospheric chemistry

The chemistry of the atmosphere is very complex. The life cycles of the atmospheric species (including traces) are strongly coupled, often in unexpected ways. Depending on the lifetime of atmospheric species, they can exhibit an enormous range of spatial and temporal variability, but every substance emitted into the atmosphere is eventually removed so that a biogeochemical cycle is established.[7]

In order to estimate the lifetimes of pollutants in the atmosphere different removal options have to be considered, and for this, the development of a reliable kinetic database for atmospheric reactions is of extreme importance. By knowing the activation energy and rate constant of every reaction taking place in the atmosphere, it would be possible to predict the chemical destiny of all compounds emitted to or generated in the atmosphere. This knowledge would also permit the estimation of the lifetime of every atmospheric species so that it would be possible to foresee their degree of migration into the different atmospheric regions, and their potential consequences. Unfortunately such experimental studies are often difficult to achieve and therefore theoretical predictions are an important alternative.

The OH radical is the most important oxidant species in the troposphere during the daytime. It reacts with virtually all the atmospheric species, organic (both saturated and unsaturated compounds) and inorganic, and in many instances in the first and rate

determining step.[5a,8] The hydroxyl radical is formed mainly from three routes: the photolysis of O_3 and HONO, and from the reaction between HO_2 and NO (the most important source at mid-day). In the absence of sunlight the OH radical concentration in the troposphere is very low.[7]

The NO_3 radical, as well as the OH radical, is a strong oxidizing agent that reacts with a number of atmospheric species.[9] The reaction of NO_3 radicals with atmospheric organic molecules can lead to the formation of undesirable compounds such as: HNO_3,[10] peroxyacyl nitrates (PANs)[11] and dinitrates.[12] The only primary source of NO_3 in the troposphere requires the simultaneous presence of NO_2 and O_3 in the same air mass, but during the day NO_3 radicals photolize rapidly, thus its presence in the troposphere is only significant at night.

Aldehydes play an important role in the chemistry of the polluted troposphere.[5a] They are emitted as primary pollutants from partial oxidation of hydrocarbon fuels, and besides, they arise as secondary pollutants from the oxidation of volatile organic compounds. Once in the atmosphere, aldehydes either photolyse or react further with OH radicals during the day, or with NO_3 radicals during the night.

Formaldehyde (HCHO) and acetaldehyde (CH_3CHO) are the most abundant aldehydes in the atmosphere and furthermore, have been regulated as hazardous air pollutants. The reactions of CH_3CHO with OH and NO_3 lead to the formation of PAN (peroxyacetylnitrate), a strong eye irritant, with phytotoxic properties and mutagenic and carcinogenic activity,[13] that has been identified as a component of photochemical smog.[5a,14]

Formyl fluoride (FCHO) is one of the halogenated molecules in the upper stratosphere, and a major product of the degradation in the troposphere of CH_3CFH_2 (HFC-134a).[15] It is also a product of the subsequent dissociation of fluorinated radicals that originate in the atmosphere. Formyl chloride (ClCHO) is a reactive molecule that forms as an atmospheric degradation intermediate of several chlorinated hydrocarbons such as

CH_3Cl, CH_2Cl_2, $CHCl_3$, and hydrochlorofluorocarbons (HCFCs),[16] as well as from the tropospheric reaction of Cl atoms with volatile organic compounds such as isoprene.[17]

The reactions of aldehydes with OH and NO_3 radicals are supposed to be tropospheric removal routes for these compounds during the day and night, respectively.

Rate constants and Arrhenius parameters for the OH reaction with a variety of aldehydes have been measured[5a,18] but there are serious uncertainties as to the reaction mechanism. For the CH_3CHO reaction the negative temperature dependence of the rate constant is well established; the activation energy of the HCHO + OH reaction is known to be almost zero, most experimental results varying between +0.7 and –1.9 kJ/mol. For the OH hydrogen-abstraction reaction from FCHO and ClCHO only experimental upper-bound rate constants have been reported and activation energy values are unknown.[19]

There have been fewer kinetic studies on the reactions of NO_3 with aldehydes than on the corresponding reactions with OH radicals. The activation energy of the NO_3 reaction with CH_3CHO has been the only one determined among the previously mentioned aldehydes. Rate constants have been reported for HCHO and CH_3CHO, but no kinetic data is available for FCHO and ClCHO. Furthermore, no previous theoretical determinations of the kinetic parameters for NO_3 reactions with aldehydes have been published.

In the first part of the thesis, the OH and NO_3 hydrogen-abstraction reactions from the above mentioned aldehydes (XCHO: X = F, Cl, H, CH_3) are studied to clarify aspects concerning the reaction mechanism and to provide accurate theoretically determined kinetic parameters. High-level *ab initio* calculations are performed with large basis sets and furthermore, transition state theory (TST) including tunneling corrections is applied to the calculation of rate constants. The results for the OH reactions are presented in Chapters 4 and 5,[20] and the NO_3 kinetic results are discussed in Chapter 6.[21] Chapter 3 provides general background information to complement the kinetic calculations reported in Chapters 4 to 6, including an overview of the concepts and approximations related to TST and tunneling calculations, among other kinetic topics.

Dr. J. Raúl Alvarez-Idaboy, presently at the Mexican Petroleum Institute (IMP) co-supervised the work presented in Chapters 4 and 5. The results discussed in Chapter 4 are part of a collaboration that also included Dr. Annik Vivier-Bunge at the Autonomous Metropolitan University (UAM - Iztapalapa), in Mexico City.

1.4. Polycyclic aromatic compounds and the interest in their study

Polycyclic aromatic hydrocarbons (PAHs) are aromatic compounds containing only carbon and hydrogen atoms in a series of inter-connected rings. They are called benzenoid or non-benzenoid depending on the presence or absence of six-membered rings. Some examples are shown in Fig. 1.1. The alkyl-, amino-, halogen- and nitro-substituted derivatives, along with the mono- and poly- N, S and O heteroatomic analogues of PAHs constitute a much larger and diverse class of molecules, the polycyclic aromatic compounds (PACs).[22]

PACs are found in both natural materials such as crude oil, and man-made substances such as engine exhaust. These substances can be useful, for example, in raising the octane rating of gasoline, but they can also be quite harmful, often possessing carcinogenic or mutagenic properties.

Syncrude Canada, located in Alberta, is a petroleum company which converts Athabasca oil sands into synthetic crude oil. It is the world's largest producer of oil made from oil sands, the largest known petroleum reserve in Canada. The petroleum industry is vitally interested in the identification and quantification of PACs in their source materials, final products and intermediate process streams, because these compounds interfere with petroleum refining operations, poisoning catalysts or building up in chemical reactors. They may also corrode refinery equipment and alter the odour and shelf lifetime of the final products. Federal environmental regulations to reduce toxic emissions also must be considered. This is of even greater importance in the oil sands industry since the aromatic content of these source materials is much higher than in most other forms of crude oil.

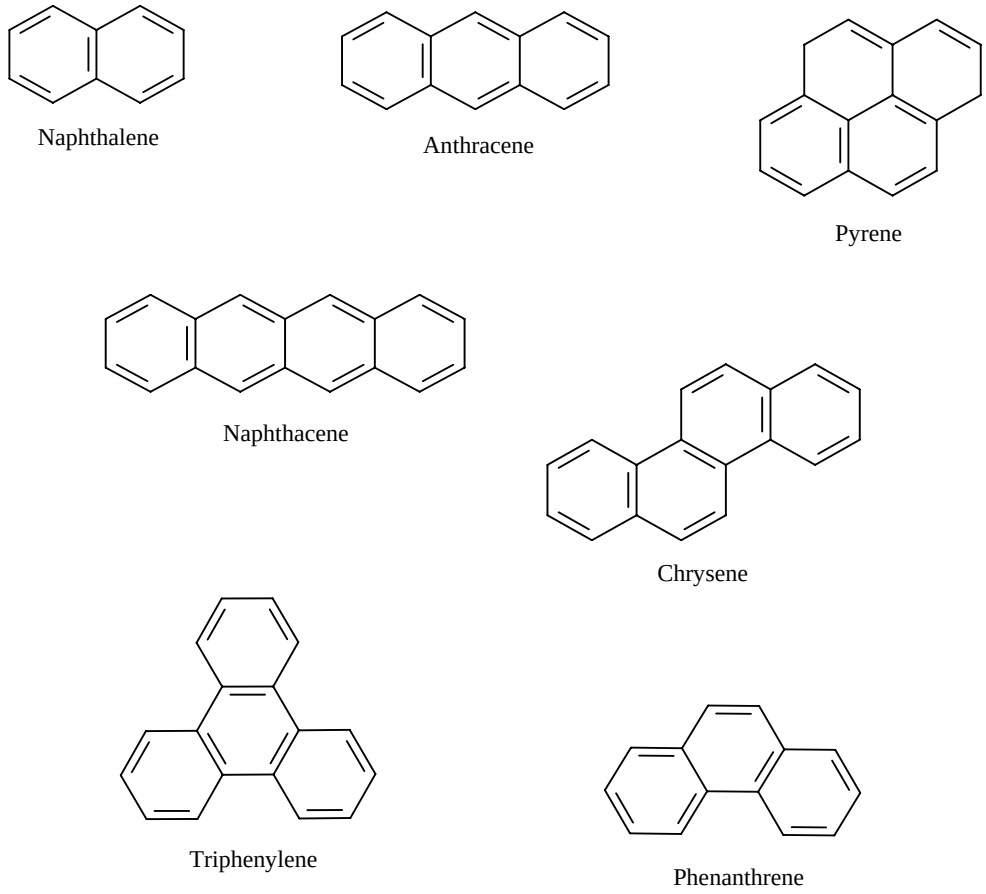

Figure 1.1. Examples of PAHs

The characterization of PACs in petroleum-related samples is extremely difficult because these samples contain thousands of such compounds which are very similar to one another and must be separated before identification. Even if complete separation were possible, identification would still be difficult because in many cases standard compounds are not available for comparison and positive identification purposes. It is in such cases that theoretical methods can play an important role as a predictive tool, since only a starting structure is needed to predict molecular properties using quantum chemistry.

It has been proposed that PACs in these samples are basically alkylated PAHs, mainly methyl- and ethyl- substituted PAHs, although it has also been suggested that partially hydrogenated PAHs may be present as a consequence of the reduction process undergone by the samples during the industrial treatment.[23] The presence of alkyl groups causes some problems in the identification of the species. The bigger the PAH the larger the number of alkylated isomers, and the greater the labour of separation, identification and quantification. State-of-the-art chromatographic methods are mainly used to separate and identify these compounds, using ultraviolet-visible (UV-vis), laser fluorescence and mass spectrometric detectors. But all these isomers are indistinguishable from each other using mass spectrometry and there are few good reference electronic spectra available.

In the second part of the thesis, Chapter 7 presents general theoretical aspects of UV-vis spectroscopy, common characteristics in the absorption spectra of PAHs, and some *ab initio* and semi-empirical methods used to calculate excited states of organic systems. The results of the calculations are outlined and discussed in Chapter 8 that focuses on the effect of alkyl substituents on the excited states of naphthalene, the smallest PAH. The effect of methyl and reduced-ring substituents (cyclic substituents which are completely reduced) on the electronic spectrum of naphthalene is examined.[24]

This study was part of a multidisciplinary project to assist Syncrude in the identification of the PACs and in tracking the progress made in improving their product. This Syncrude project was a collaboration with the research groups of Drs. R. D. Guy, L. Ramaley and P. D. Wentzell. Dr. Guy's group was responsible for the development and optimization of liquid chromatographic techniques to give the best possible separation of the compounds present in the complex test mixtures. Dr. Ramaley's group was in charge of the construction, development, calibration and optimization of the detection schemes which include a laser fluorescence detector and the use of a quadrupole mass spectrometer. The group of Dr. Wentzell uses the chromatographic data to assist in the identification of poorly resolved compounds by using chemometric methods. The theoretical contribution was intended to provide calculated data related to the chemical-physical properties of PACs, to assist or complement the work done by the other groups.

Chapter 9 will present global conclusions and plans for future work on the previously mentioned topics.

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