Chapter 9. Global Conclusions and Future Work

9.1. OH and NO_3 hydrogen-abstraction reactions from aldehydes

*9.1.1. **Global conclusions***

The main conclusion of this study is that in the gas phase there are no elementary bimolecular reactions (in which a TS is formed) because a reactant complex is always initially formed, even though in some cases its formation is irrelevant. The consideration of the reactant complex formation is especially important in radical-molecule reactions, many of which are known to occur with an apparent negative activation energy.

It can also be rationalized from the present results that the bigger the effective energy barrier for radical-molecule reactions, and the smaller the stabilization energy of the reactant complex, the more closely its behaviour resembles an elementary reaction. In other words, two extreme behaviours can be considered for a radical-molecule reaction: for systems with very low or negative activation energies the consideration of a complex mechanism is essential (as in the case of the OH + aldehyde reactions), but if the activation energy is significantly higher and the stabilization energy of the reactant complex is negligible, then the consideration of an elementary process will be a satisfactory approximation. This situation was made evident in the study of the NO_3 hydrogen-abstraction reactions for which it was shown that the formation of the reactant complex could be ignored.

After being able to establish computational methodologies to reproduce the experimental kinetic and thermodynamic parameters of the two groups of reactions studied, better or new theoretically determined quantities were obtained for reactions for which incomplete or no kinetic information is available. The predictive capability of the combination of *ab initio* methods with TST, considering Eckart corrections for tunneling, has been demonstrated.

9.1.2. ***Suggestions for future work***

Even though only TST with Eckart tunneling corrections were applied in these studies, it would be interesting to test how other more sophisticated theories behave in predicting the rate constants of the reactions studied.

If the equilibrium constant for the reactant complex formation, K_{eq}, and the rate constant of the hydrogen-abstraction process, k_2, were to be reported, they need to be corrected by considering the internal rotations generated in the reactant complex.

The incorporation of tunneling effects in the calculation of activation energies and pre-exponential factors for the reactions in which tunneling was estimated to be significant, would be interesting. It will require the calculation of rate constants at temperatures around 298 K and the construction of a lnk *versus* 1/T plot (or by obtaining the corresponding analytical expression). From the slope and the intercept of the tangent to the above mentioned curve at the desired temperature, the Arrhenius parameters may be determined. This procedure will allow the determination of the pre-exponential factors for the reactions of FCHO and ClCHO with OH and NO_3, which are not known experimentally. In fact, such a program was written by the author in FORTRAN language but still needs to be tested for systems in which free internal rotations are considered to correct the total partition function of the TS. This program has already been used to obtain Arrhenius plots for the intramolecular hydrogen transfer in polymers, as a project in collaboration with Dr. Jesus M. Ugalde at the University of the Basque Country, in Spain.

Preliminary calculations on the NO_3 radical at the B3LYP/6-311G(d,p) level show that the D_{3h} structure is predicted to be the ground state minimum. CCSD(T) single point calculations using the previous geometry and basis set gives a similar result, although the difference in energy with the other C_{2v} structures is very small. This result is in correspondence with the fact that in the B3 functional less HF exchange is considered in comparison with the BH&H functional. This suggests that maybe B3LYP optimized

geometries and frequencies could be used for kinetic studies on reactions with the NO_3 radical. For the reaction of acetone with NO_3, only an upper bound rate constant has been reported, hence, this could be another interesting system to work on.

9.2. Effects of alkyl substituents on the excited states of naphthalene

*9.2.1. **Suggestions for future work***

A series of mono-, di-, tri- and tetra-methylnaphthalenes have already been studied in order to determine if there is a correlation between the pattern of substitution, the degree of perturbation of the molecular orbitals, and the UV-visible bands of these compounds. Geometry optimizations were performed at different levels of theory: AM1, HF and B3LYP, and excited states were obtained by means of the semiempirical ZINDO/S method. Principal component analysis (PCA), a multivariate technique, has been shown to provide important insight into establishing such correlations when large sets of theoretical data are analysed. Isomers with the same pattern of substitution have shown very similar UV-visible spectra because their MOs are perturbed in a similar way. The above study could be extended to all the tri- and tetra-methylnaphthalenes.

The probability densities of certain MOs and the composition of the calculated excited states (in terms of the dominant singly excited configurations) can also help rationalize the effects of different substituent positions on the perturbation of MOs and the position of the UV-visible maxima.

Ultraviolet detection in high performance liquid chromatography (HPLC) is particularly useful for PACs, especially in non-polar solvents. Fluorescence detection in HPLC is a more frequently used technique for these compounds than UV-visible detection. Hence, the prediction (calculation) of fluorescence spectra of PACs would be very useful to assist in the separation and identification of these compounds, particularly since all the standards needed to validate the identifications are not available.

When absorption spectra are measured in solvents of increasing polarity it is found that the position and intensity of absorption bands change. Fluorescence spectra are more dependent on the environment and greater changes are produced with the change of solvent. Solvent effects have been ignored in this study (calculations have been done in the gas phase), but more realistic predictions require their consideration.