Reactivity Trends in Radical-Molecule Tropospheric Reactions – A Quantum Chemistry and Computational Kinetics Approach

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1. Introduction

The most relevant chemical reactions that take place in the atmosphere involve free radicals and volatile organic compounds (usually termed VOC). In the troposphere, the main sink of volatile organic compounds (VOC) is oxidation, initiated typically by reaction with hydroxyl (OH) free radicals. Many of these processes give rise to the formation of new radicals, which ultimately cause higher OH radical levels and thus higher rates of reactions of the other VOC present.

Kinetic investigations of the OH radical reaction with VOC's are essential for the evaluation of their significance in air pollution. Reaction rate coefficients are used, for example, in estimating their tropospheric lifetimes, or in atmospheric chemical model calculations which are used to generate distribution maps of air pollutants under given meteorological and topographical conditions. Furthermore, the use of temperature dependent reaction rate coefficients in model calculations increases their accuracy, since the temperature gradient of the troposphere and the seasonal temperature variations can be taken into consideration.

As a result of almost three decades of research, the rate constants and mechanisms of the initial reactions of OH and NO_3 radicals with VOCs are now reliably known or can be estimated. Significant advances have been made in our understanding of the mechanisms of the reactions subsequent to the initial OH and NO_3 radical attack on selected VOCs and of first-generation products formed from these reactions. Extensive and comprehensive reviews on the current state of knowledge of atmospheric reactions of VOCs have been written periodically over the years. Modern rate constant measurements are often precise, and individual values are known fairly well. In addition, methods exist for estimating rate

constants for the reactions of VOCs with OH and NO$_3$ radicals which can be used when data are not available. A realistic uncertainty estimate for most VOCs is a factor of 2. Data concerning rate constants for the reactions of the radical intermediates are much more limited and are usually restricted to the simplest cases. It has been assumed that the higher molecular weight radicals react with the same rate constant as their low molecular weight counterparts.

Theoretical calculations provide the data needed to support application of thermochemically-based estimation methods and to evaluate proposed reaction sequences. Estimates of reaction heats and free energies are also used to rule out chemically unreasonable reaction schemes. In recent years the development of theoretical methods for the calculation of potential energy surfaces has led to the direct computation of rate constants. These computational techniques have been tested by comparison with available data for known reactions, and then applied to understand and predict mechanisms and reaction rates. In addition, computational methods provide a useful tool for reducing the time required in the laboratory by suggesting specific product compounds for analysis in chamber experiments. For example, for many combustion systems, detailed kinetic models often consist of up to several thousands of elementary reactions whose kinetic parameters are mainly estimated from those available for similar reactions. Computational kinetics affords one of the simplest and most cost-effective methods for calculating thermal rate constants, by applying the conventional transition state theory (TST), which requires only structural, energetic, and vibrational frequency information for reactants and transition states. On the basis of the TST framework, much progress has been made in developing direct ab-initio methods for calculating rate constants from first principles.

For the last decade the main emphasis of our research in atmospheric chemistry has been to investigate mechanisms and kinetics of many different atmospherically important reactions of selected VOCs and of their reaction products. In particular, we have studied the OH and NO$_3$ initiated oxidation of several groups of organic compounds (alkanes, alkenes, dienes, aromatics, aldehydes, carboxylic acids, alcohols, ethers, etc.) under tropospheric conditions, as well as water-assisted reactions and heterogeneous processes in the presence of mineral aerosol surfaces.

One of our major findings has been the correct explanation of the anti-Arrhenius behavior that is common to many radical-molecule reactions. Indeed, many of these reactions present negative activation energies, i. e. their rate constant decreases with increasing temperature. Following the suggestion of Singleton and Cvetanovic proposed in 1976 (Singleton & Cvetanovic, 1976) and using quantum chemistry methods, we showed that the existence of a stable Van der Waals pre-reactive complex in the entrance of the reaction channel explains satisfactorily the observed kinetic data. Thus, radical-molecule reactions must be seen as complex reactions consisting of more than one elementary step. This mechanism and the resulting rate constant expression are derived in the next Section.

Heterogeneous processes that involve the impact of aerosols and trace vapors on the VOC atmospheric chemistry is a fairly new field of research, and its importance has steadily grown due to its environmental importance. Laboratory studies, together with field observations and modeling calculations, have clearly demonstrated the importance of heterogeneous processes in the atmosphere. In this sense, it is very important to understand the role of particulate matter and the extent to which heterogeneous reactions on solids as

well as multiphase reactions in liquid droplets contribute to the atmospheric chemistry. For example, the potentially reactive surface of mineral aerosols may be a significant sink for many volatile organic compounds in the atmosphere, and consequently it could influence the global photooxidant budget. In addition, the special nature of H_2O as a third body may need to be taken into account.

In this work, we summarize the theoretical methodology employed in our work to study the mechanisms and kinetics of the reaction of a variety of COV with OH radicals, in the gas phase and in the presence of mineral aerosols. Also, the possibility of single-water molecule catalysis of OH reactions with volatile organic compounds is discussed.

2. Theoretical methodology

Ab initio quantum chemical calculations can provide results approaching benchmark accuracy for small molecules in the gas phase (Martin & de Oliveira, 1999) and they have proven to be very useful to complement experimental studies. Small molecules in the gas phase are typically addressed by high-level methods such as CCSD(T), QCISD(T) and MRCI, which in many cases are as accurate as experiments (Friesner, 2005). A wide variety of properties such as: structures (Thomas, 1993); thermochemistry (Guner, 2003); spectroscopic quantities (Stanton & Bartlett (1993); and kinetics (Fernandez-Ramos, 2006) can be effectively computed.

In this section, a summary of the theoretical methodology employed in our work since 1994, and a discussion of the various methods in connection with the kinetics calculations of tropospheric reactions, is presented.

Electronic structure calculations have been performed using MP2 and DFT methods. The reliability of DFT methods to properly describe chemical reactions has been discussed elsewhere (Siegbahn & Blomberg, 1991; Fernandez-Ramos, 2006).

Although the calculations performed in the atmospheric chemistry related to the VOC oxidation cover a list of different quantum chemistry methods that have been used over the years, our latest work has been performed using the M052X density functional method (Zhao, 2006) developed specifically for kinetic calculations by Professor Truhlar and his group. The M05-2X functional has been parametrized to take into account dispersion forces. This functional has previously been tested to model complex reactions, and it has been shown that it provides excellent structures, energies and kinetics results at a reasonable computational cost, thus allowing treatment of large systems (Vega-Rodriguez & Alvarez-Idaboy (2009).

2.1 B//A approach

We have used a procedure that has become common in the study of the stationary points of chemical reactions of polyatomic systems because it is relatively inexpensive from a computational point of view and it usually reproduces correctly the main features of the reaction path. It is known as B//A approach, and it consists of geometry optimizations at a given level (A) followed by single point calculations, without optimization, at a higher level (B). Based on our previous experience, the use of B//A approach at CCSD(T)//BHandHLYP level of theory properly describes the energetic and kinetics

features of VOCs + OH hydrogen abstraction reactions. In addition, for this kind of reactions it has been proved that the differences in geometries between several DFT methods compared to CCSD and QCISD are minimal for BHandHLYP (Szori, 2006). However in some of our earlier works other methods were used. More recently in the Truhlar group (University of Minnesota) new DFT methods have been developed that can achieve the required accuracy for kinetic and thermodynamic calculations without the need of refining energies with post Hartree-Fock methods. This is the case of the M05-2X functional that we have adopted for some of our recent studies (Zavala-Oseguera et al., 2009; Galano et al. 2011, Galano & Alvarez-Idaboy, 2009; Pérez-González & Galano 2011; Leon-Carmona & Galano, 2011; Galano 2011; Gao et al., 2010; Iuga, et al. , 2010, Iuga et al. 2011).

In some cases the results obtained with this functional are closer to experimental results than the ones obtained at the CCSD(T)//BHandHLYP level.

2.2 Free radical kinetics

We present here a brief overview on the methodology used to compute the rate constants in the examples that are going to be discussed later. For a chemical reaction that occurs through a stepwise mechanism involving the formation of a reactant complex in the entrance channel, at least two steps must be considered in the kinetics, namely: (1) the formation or the reactant complex from the isolated reactants, and (2) the formation of the products from the reactant complex. For VOCs + OH reactions that mechanism can be written as:

$$VOC + OH\bullet \; \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \; [VOC \text{ ---- } OH]\bullet \; \overset{k_2}{\longrightarrow} \; Products$$

Provided that $k_{-1} + k_2 > k_1$, i.e, the complex rapidly disappears, a steady-state analysis leads to a rate coefficient for each overall reaction channel which can be written as:

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (1)$$

In general the energy barrier for k_{-1} is about the same size as that for k_2, in terms of enthalpy. However, the entropy change is much larger in the reverse reaction than in the formation of the products. The activation entropy ΔS_2 is small and negative because the transition state structure is tighter than the reactant complex, while ΔS_{-1} is large and positive because six vibrational degrees of freedom are converted into three translational plus three rotational degrees of freedom. This leads to k_{-1} values that are much larger than k_2. Based on this assumption, first considered by Singleton and Cvetanovic, the overall rate coefficient (k) can be rewritten as:

$$k = \frac{k_1 k_2}{k_{-1}} = K_{eq} \cdot k_2 \qquad (2)$$

where k_2 is the rate constant corresponding to the second step of the mechanism, i.e., transformation of the reactant complex into products; and K_{eq} is the equilibrium constant between the isolated reactants and the reactant complex. Applying basic statistical

thermodynamic principles the equilibrium constant (k_1/k_{-1}) of the fast pre-equilibrium between the reactants and the reactant complex may be obtained as:

$$K_{eq} = \frac{Q_{RC}}{Q_R} \exp\left[(E_R - E_{RC}) / RT\right]$$ (3)

where Q_{RC} and Q_R represent the partition functions corresponding to the reactant complex and the isolated reactants, respectively.

Let us emphasize that when it is claimed that the reactant complexes are lower in energy than the isolated reactant, this statement is made in terms of enthalpy or ZPE corrected electronic energies. On the other hand, the Gibbs free energy associated with step 1, i.e, the formation of the reactant complex ($G_1 = G_{RC} - G_R$), is always positive in a wide range of temperatures around 300 K. The expression for the equilibrium constant can also be written as:

$$K_{eq} = \frac{k_1}{k_{-1}} = \exp\left(-\Delta G_1 / RT\right)$$ (4)

From this expression, it is evident that $K_{eq} < 1$ for endergonic processes ($\Delta G_1 > 0$), i.e. $k_{-1} > k_1$, which validates the steady state hypothesis.

On the other hand k_2 can be calculated within the frame of the Transition State Theory. A typical reaction profile for this kind of reactions, in terms of Gibbs free energy and enthalpy, is shown in Figure1.
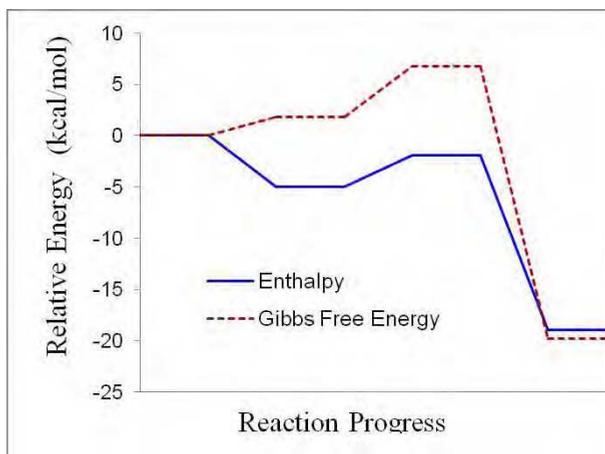

Fig. 1. Typical energy profiles, at 298.15 K, in terms of enthalpies and Gibbs free energies, of an atmospheric reaction with negative activation energy..

2.3 Conventional transition state theory (CTST)

From a phenomenological point of view, numerous experiments have shown that the variation of the rate constant with temperature can be described by the Arrhenius equation:

$$k = A \exp\left(-Ea / RT\right) \tag{5}$$

where Ea is the activation energy and A is the pre-exponential or frequency factor, which may have a weak dependence on temperature. If a reaction obeys the Arrhenius equation, then the Arrhenius plot (*ln k* versus *1/T*) should be a straight line with the slope and the intercept being *-Ea/R* and *A*, respectively.

In a unimolecular process, under high-pressure conditions, an equilibrium distribution of reactants is established and the Transition State Theory formula can be applied to calculate k_2:

$$k_2 = \sigma \kappa_2 \frac{k_B T}{h} \frac{Q_{TS}}{Q_{RC}} \exp\left[\left(E_{RC} - E_{TS}\right) / RT\right] \tag{6}$$

where σ is the symmetry factor, which accounts for the number of equivalent reaction paths, κ is the tunneling factor, k_B and h are the Boltzmann and Planck constants, respectively, Q_{TS} is the transition state partition function, and the energy difference includes the ZPE corrections. In this approach the reactant complex is assumed to be in its vibrational ground state.

In a classical treatment the influence of the complex exactly cancels in equation 2 and the overall rate coefficient depends only on the properties of OH, VOCs, and the transition states. However, when there is a possibility of quantum mechanical tunneling, the existence of the complex means that there are extra energy levels from where tunneling may occur so that the tunneling factor increases. Since it has been assumed that a thermal equilibrium distribution of energy levels is maintained, the energy levels from the bottom of the well of the complex up to the barrier might contribute to tunneling.

2.4 On the Basis Set Superposition Error (BSSE) dilemma

One issue of concern when modeling weakly bonded systems is the BSSE, which is caused by the truncation of the basis set. From a theoretical point of view its existence has been well established (Mayer, 1983; Vargas et al., 2000; Mayer, 1996). It is especially important in weakly bound complexes such as Van der Waals and hydrogen-bonded complexes and transition states, because for these systems the BSSE and the binding energies are of the same order of magnitude. The most widely used and simplest way to correct BSSE is the counterpoise procedure (CP) (Jansen & Ros, 1969; Boys & Bernardi, 1979). In CP, for a dimer system formed by two interacting monomers: CP², the BSSE is corrected by calculating each monomer with the basis functions of the other one (but without its nuclei or electrons), using so-called "ghost orbitals". However, the use of this method is polemic since several authors have proposed that it overestimates the BSSE (Frisch et al., 1996; Schwenke & Truhlar, 1985; Morokuma & Kitaura, 1981; López et al., 1999; Hunt & Leopold, 2001; Valdés & Sordo, 2002a, 2002b).

It has been pointed out by Dunning (Dunning, 2000) that "It is quite possible and even probable that the binding energies computed without the counterpoise correction are closer to the complete basis set limit than the uncorrected values. This situation is due to the fact that BSSE and basis set convergence error are often of opposite sign." Since it cannot be established *a priori* if that is the case, we have modeled the closest system to our reactant
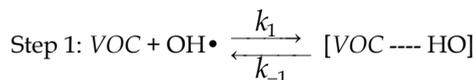
complexes with known experimental binding energy: the water dimer. The experimental value for the electronic dissociation energy (*DE*) of water dimer is 5.4 kcal/mol. We have modeled the water dimer at the CCSD(T)//BHandHLYP/6-311++G(d,p) level and *DE* values of 5.2 and 3.9 kcal/mol are obtained without and with CP² corrections, respectively. The CP uncorrected value is closer to the experimental one, suggesting that for the water dimer, at this level of calculation, the BSSE and Basis set truncation errors cancel each other. Since the reactant complexes between oxygenated VOCs and OH radicals are formed in an equivalent chemical way, i.e they are formed trough the interaction of the H atom in the OH radical and an oxygen atom in the VOCs, and as it will be discussed later they also have electronic binding energies that are very similar in magnitude to that of the water dimer, it is reasonable to assume that the same cancellation of errors occurs in our systems.

Recently we have performed a detailed investigation on the role of the cancelation of BSSE and the Basis Set Truncation Error (Alvarez-Idaboy & Galano, 2010). We have found that the inclusion of CP corrections systematically leads to results that differ from the CBS-extrapolated ones to a larger extent than the uncorrected ones. Contrary to the general belief, this effect is more significant if only weak interactions are analyzed. Accordingly, from a practical point of view, when relatively small basis sets are used, we do not recommend the inclusion of such corrections in the calculation of interaction energies, since it may lead to values with larger discrepancies with the accurate ones. We think that the best way of dealing with BSSE, for large-sized systems that make CBS extrapolations computationally unfeasible, is not to use CP corrections, but instead to make a computational effort for increasing the basis set. This approach does not eliminate BSSE but it significantly decreases it and, more importantly, it proportionally decreases all the errors arising from the basis set truncation. This does not necessarily mean that one should use a very large basis set, as it has been interpreted by several authors, but rather only to increase the basis set. For example, instead of using 6-31G(d,p) with counterpoise correction it is better to perform 6-31++G(d,p) calculations without CP. The interaction energies obtained from the latter methodology should be closer to the experimental values than those arising from using the first one.

3. Gas phase reactions

In this section, we will discuss the most important trends in the reactivity of VOCs towards OH free radicals in the gas phase.

In most radical–molecule reactions, a complex two-step reaction mechanism is assumed, which involves the formation of reactant complexes that are in equilibrium with the separated reactants, followed by an irreversible step that leads to the products:

$$\text{Step 1: } VOC + \text{OH} \bullet \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [VOC \text{----} \text{HO}]$$

$$\text{Step 2: } [VOC \text{---} \text{HO}]^{\cdot} \xrightarrow{k_2} Products$$

In H-abstraction reactions, the corresponding radical and one water molecule are formed, while in the OH-addition reactions, an adduct is formed. In general, in saturated and oxygenated VOCs oxidations, H-abstraction is the most important mechanism, while the

predominant mechanism in unsaturated VOCs oxidation is OH-addition. In general, branching ratios may change as a function of temperature.

3.1 H-abstraction

Hydrogen abstraction of saturated hydrocarbons by the hydroxyl radical is one of the most important classes of reactions in combustion chemistry. This is clear from the more than 70 experiments and theoretical studies that are available in the literature for the smallest reaction in this class, namely, the OH$\cdot$ + CH_4 = H_2O + $\cdot CH_3$ reaction. However, kinetic information for reactions involving larger hydrocarbons, for example, larger than C5, is limited.

In urban air, oxygenated compounds represent about 20% of the emitted VOCs. They are also formed in situ in the atmosphere from the oxidation of other VOCs.

The reactions of OH radicals with oxygenated compounds in the gas phase seem to proceed via formation of complexes that involve one or two hydrogen bonds. Several theoretical studies on these complexes show binding energies large enough to overcome any inaccuracy of the calculation method. In particular, the relevance of including such complex in the modeling of oxygenated VOCs + OH reactions has been discussed in detail (Galano & Alvarez-Idaboy, 2008). Taking them into account, together with any possible intramolecular interaction in the transition states structures, leads to very reliable theoretical values of the
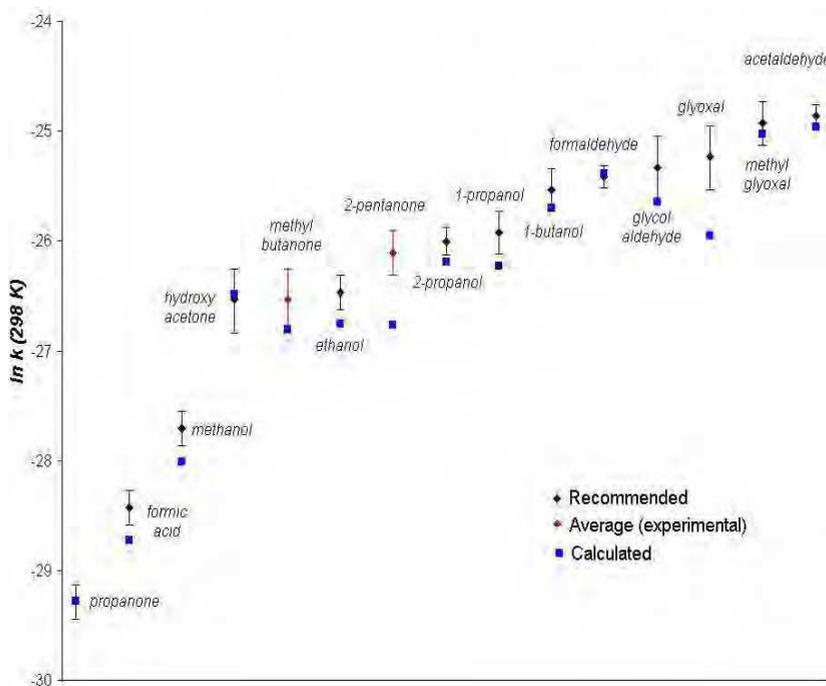

Fig. 2. Comparison between recommended experimental, and calculated rate coefficients, at 298 K.

rate coefficients. To prove this statement, Figure 2 shows a comparison between calculated rate coefficients, at 298 K (Alvarez-Idaboy, 2001; Galano et al. 2002a; Alvarez-Idaboy et al., 2004; Galano et al. 2002b; Galano et al., 2004; Galano et al., 2005; Galano, 2006) for several VOCs + OH reactions and recommended values (Atkinson et al., 1999). For 2-pentanone and methylbutanone there are no recommendations, therefore the average from the experimental values was used instead for 2-pentanone, and the only experimental value available for methylbutanone. As this figure shows, the calculated rate coefficients are in excellent agreement with the available experimental data. The calculated values are within the error range from experimental determinations in most of the studied cases. The largest discrepancies were found for glyoxal and 2-pentanone, which differ from the recommended values in 51 and 48 %, respectively. Even for them the agreement is very good, since an error of 1 kcal/mol in energies represent about one order of error in the rate constant, and in all the cases the discrepancies are smaller than that. Accordingly, the calculated results in Figure 2 can be considered within the error inherent to the most accurate quantum mechanical calculations, or even smaller.

All the main conclusions from these articles are now accepted in recent works (Tyndall et al., 2002) and it is well known that hydrogen abstraction is the main reaction channel if not unique (Butkovskaya et al., 2004).

3.2 OH-addition

OH-addition channel is the dominant pathway in unsaturated VOCs oxidation. In the troposphere, alkenes participate in a sequence of reactions which ultimately lead to their breakdown into highly toxic aldehydes, at the same time altering the equilibrium ratio of nitrogen oxides and indirectly producing ozone.

The mechanism of the reaction has been studied in our group for several alkenes from a theoretical point of view. Initially we obtained the potential energy surface of the propene + OH reaction, both in the presence (Dıaz-Acosta et al., 1999) and in the absence of oxygen, (Alvarez-Idaboy et al., 1998), and the preferred site for addition of OH and O_2. A complex mechanism involving the formation of a reactant complex was postulated to explain the observed negative activation energy. An interesting finding was the elucidation of the branching ratios in the propene–OH reaction. According to the results, the apparent discrepancy between thermochemical data (which favor addition of the OH radical to the central carbon atom of propene) and experimental results obtained indirectly from a product study (which finds that 65% of the final products are consistent with addition of OH to the terminal carbon) can be explained if one also considers the subsequent reaction (OH–propene) + O_2. At atmospheric pressure, addition at the central carbon atom is energetically favored, both in terms of barrier heights and of heats of formation of the products, although differences in energy between the two pathways are quite small (less than 2.5 kcal/mol), implying, in fact, that both channels should occur. However, a crossing occurs between the energy profiles when O_2 is added, favoring, by as much as 4.0 kcal/mol, addition of O_2 to the less stable OH–propene adduct. The branching ratio of both reactions, with the predominance of one isomer over the other, is expected to be both pressure and temperature dependent. In addition, a study of the temperature dependence of the rate constant for the O_2 addition reaction should yield a different slope for reactions to both initially formed adducts.

Later, in a more detailed study that included rate constant calculations (Alvarez-Idaboy et al., 2000), it was possible to explain the origin of the negative activation energy observed in experiments. We concluded that, when the OH + alkene reaction occurs at atmospheric pressure, the following hold:

- The reaction is not elemental.
- The overall addition of OH is irreversible, due to the large thermal effect of reaction that is usually larger than 30 kcal/mol.
- The overall rate depends on the rates of two competitive reactions: the reverse of the first step and the second step, the former one being more affected by temperature than the latter.

We showed that only Singleton and Cvetanovic's[6] hypothesis is compatible with the above three points, i.e., the existence of a relatively stable pre-reactive complex, in equilibrium with the reactants, and from which the addition adduct is formed irreversibly. However, the activation energy of the OH-alkene reactions at high pressures can be calculated as the difference between the energy of the TS and that of the reactants, without having to obtain the pre-reactive complex. This hypothesis and methodology proposed for the first time in OH + alkene reactions was later used to explain the mechanisms and kinetics of many other addition reactions and was the basis for the study of other atmospheric reactions (Francisco-Márquez et al., 2003; Francisco-Márquez, et al., 2004; Francisco-Márquez et al. 2008; Vega-Rodriguez & Alvarez-Idaboy, 2009).

In a series of studies on OH reactions with aromatic hydrocarbons (Uc et al. 2000; Uc et al.,2001; Uc et al. 2002; Uc et al. 2004; Uc et al. 2006; Andino & Vivier-Bunge, 2008) we showed that pathways involving the initial formation of *ipso* adducts might also play a non-negligible role in tropospheric chemistry (Figure 3). In general, only addition to *ortho, meta,*
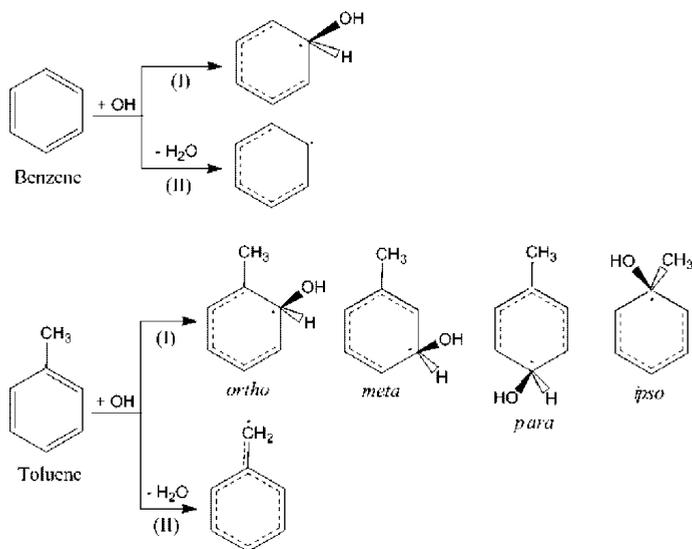
Scheme I

Fig. 3. Possible channels in OH addition to benzene and toluene.

and *para* positions have been considered in laboratory studies for OH/aromatic systems. However, only about 70% of the reacted carbon has been fully accounted for. Trayham (Trayham,1979) described numerous examples of ipso free radical substitution and he emphasized the importance of the ipso position in free radical reactions with aromatic hydrocarbons. Tiecco (Tiecco, 1980) showed that radical additions to ipso sites could be important, or even more important, than addition to the nonsubstituted carbon sites of aromatic compounds. Rather than a steric hindrance, stabilization due to interactions between the lone pair on the oxygen atom and two methyl hydrogen atoms has been described in some of these studies. In the case of toluene reaction with OH, we estimated that ipso addition contributes 13% to the overall reaction. Results have been summarized in (Andino & Vivier-Bunge, 2008).

3.3 Competing mechanisms

In some reactions, competing channels occur, and different mechanisms are favored depending on temperature. This is the case for benzene and toluene, where three distinct regions can be observed in the Arrhenius plots of log *k* versus $1000/T$ (Finlayson-Pitts & Pitts, 1986). At low temperatures, below 325 K, the plot is linear but with a slope that is negative for benzene and positive for toluene. At temperatures above 380 K, a linear plot is obtained with a negative slope, typical of a normal Arrhenius behavior. Between these two temperatures, a non-exponential decay is observed (Perry et al. 1977; Tully et al., 1981) and the Arrhenius plot presents an abrupt discontinuity. There are no recommended values for the rate constants in this region. The Arrhenius plot for toluene +OH is shown in Figure 5.

The existence of the positive slope in the low-temperature region in the toluene reaction, which implies that the observed activation energy is negative, can be explained in terms of a complex mechanism that has been discussed in Section 2. The non-exponential OH decay in the intermediate temperature region and the unusual Arrhenius plots have been rationalized on the basis of two types of reaction paths, addition and abstraction, occurring simultaneously. It has been postulated that the thermalized OH-aromatic adduct formed by the OH radical addition to the ring decomposes back to reactants (Tully et al. 1981), thus decreasing the importance of the addition channel and leading to bimolecular reaction rate-constant values significantly lower than those measured near room temperature.

Computational kinetics calculations (Uc et al. 2008) were performed, using quantum chemistry data for these reactions under pseudo-first-order conditions, in order to explain the observed Arrhenius plots. We employed a theoretical approach that is in line with both experimental and environmental conditions and that takes into account the fact that aromatic concentrations are in large excess compared to OH concentrations. Thus, pseudo-first-order kinetics was used to describe the addition reactions, and the possibility of the reverse reaction was explicitly introduced. Branching ratios were obtained for all channels.

The study used pseudo-first-order conditions, with aromatic concentrations in large excess compared to OH concentrations as is the case both in previous experiments and in the atmosphere. Our results are in excellent agreement with the experimental data in the whole 200-600 K temperature range. They reproduce the observed non-exponential OH decay. The suggestion that the non-exponential OH decays observed in the 300 K < T < 400 K range are caused by the decomposition of thermalized OH-aromatic adducts back to reactants and the competition between abstraction and addition channels was confirmed. Moreover, we

showed that the low-temperature onset of the non-exponential decay depends on the concentration of the aromatic compounds: the lower the concentration, the lower the temperature onset. This finding could have atmospheric implications since, under atmospheric conditions, the non-exponential decay occurs in the 275-325 K range, which corresponds to temperatures of importance in tropospheric chemistry. The temperature dependence of benzene + OH rate constant at different times, for an initial aromatic concentration of $[arom]_0 = 1 \times 10^{13}$ molecule/cm^3 is shown in Figure 4.
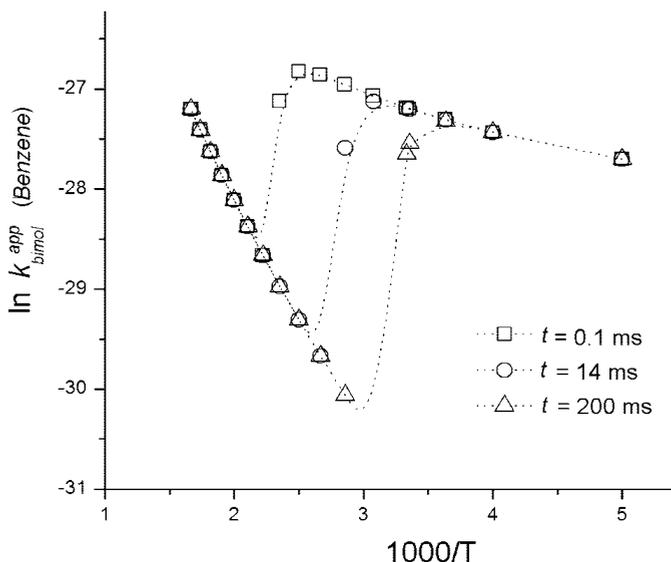
Fig. 4. Temperature dependence of benzene + OH rate constant at t = 0.1, 14 and 200 ms, for pseudo-first-order conditions with $[benzene]_0 = 1 \times 10^{13}$ molecule/cm^3

4. Water-assisted gas phase reactions

A 2007 publication in Science (Vöhringer-Martinez et al., 2007) suggested the possible role of a single water molecule in the oxidation reaction of acetaldehyde by a hydroxyl radical. The authors used a wind-tunnel apparatus with detector lasers to study the reaction between gaseous hydroxide radicals and acetaldehyde molecules (OH + $CH_3CHO \longrightarrow H_2O + CH_3O$), in the 60-300 K temperature range. They detected a small but detectable increase in the rate constant at low temperatures. Accompanying theoretical calculations showed that the complex formed between an acetaldehyde molecule and a single water molecule is more vulnerable to OH radical attack than free acetaldehyde. Indeed, the energy barrier for the complex + OH reaction is considerably smaller than for acetaldehyde + OH. A comment by I. Smith in the Perspectives Section in the same issue of Science (Smith, 2007) acknowledged the interest of this work, but questioned its relevance to atmospheric chemistry in terms of the negligibly small amount of existent water-acetaldehyde complex.
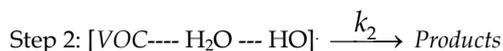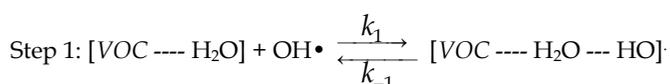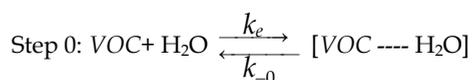
In fact, the kinetic effect of the presence of water had already been studied (Canneaux et al., 2004) in a theoretical study of the reaction of acetone with OH radicals in the presence of a single water molecule. Their conclusion was that the tropospheric concentration of OH-

acetone-water complexes would be very small, but that they might still be detected experimentally. Since then, several articles have been published suggesting possible one-molecule catalysis in reactions of OH radicals with other organic volatile compounds (Chen et al., 2008; Buszek & Francisco, 2009). All of them involve oxygenated VOC's, since, in these cases, the OH reaction transition state barriers may be considerably decreased by hydrogen bonds involving a water molecule.

There has also been considerable speculation about the role of water complexes and other hydrogen-bonded molecular complexes on the kinetics and dynamics of gas-phase free radical reactions (Luo et al. 2009; Long et al. 2010). A field measurement in the near-infrared has revealed a relatively high concentration of 6×10^{14} molecule cm^{-3} of water dimer in the atmosphere (Pfeilsticker et al. 2003). This finding has been reproduced very well by a theoretical study (Dunn et al., 2004). However, although detectable, the water dimer concentration represents only about 1% of the total water present in air in tropospheric conditions. The concentration of VOC-water complexes in air is expected to be even smaller in most cases (Galano et al. 2010), and the catalytic effect of water is therefore questionable.

In a series of articles on the reactions of acetaldehyde (Iuga et al., 2010a), glyoxal (Iuga et al., 2010b), acetone (Iuga et al., 2011a) and formic acid (Iuga et al., 2011b) with OH radicals in the presence of water, we showed that consideration of the initial water complexation step is essential in the rate constant calculation. Even if the VOC-H_2O complex + OH rate constant is often orders of magnitude larger than the VOC + OH rate constant, if very little complex is formed, the resulting rate constant will not be significantly modified.

Since the simultaneous collision of the three molecules involved (VOC + H_2O + OH) is very improbable, the termolecular mechanism is ruled out. Hence, the most probable mechanism consists of two consecutive bimolecular elementary steps, presumably complexation of the VOC with water, followed by reaction of the complex with an OH radical. Reaction with OH, in turn, has been shown to involve the initial formation of a pre-reactive complex, as discussed in Section 2. Thus, the mechanism can be written as:

$$\text{Step 0: } VOC + H_2O \xrightleftharpoons[k_{-0}]{k_e} [VOC \text{ ---- } H_2O]$$

$$\text{Step 1: } [VOC \text{ ---- } H_2O] + OH\bullet \xrightleftharpoons[k_{-1}]{k_1} [VOC \text{ ---- } H_2O \text{ --- } HO]^.$$

$$\text{Step 2: } [VOC \text{ ---- } H_2O \text{ --- } HO]^. \xrightarrow{k_2} Products$$

The most stable water complex structures formed in Step 0 with acetaldehyde, glyoxal, acetone and formic acid are shown in Figure 5, and the percent of complex formed at 298K is indicated under each structure.

When these complexes react with OH radicals, in the entrance reaction channel a termolecular pre-reactive complex is formed, which presents multiple H-bonds. In all cases the reaction path depends on the initial molecular arrangement, since various combinations are possible. These termolecular complexes are in general very stable because they involve
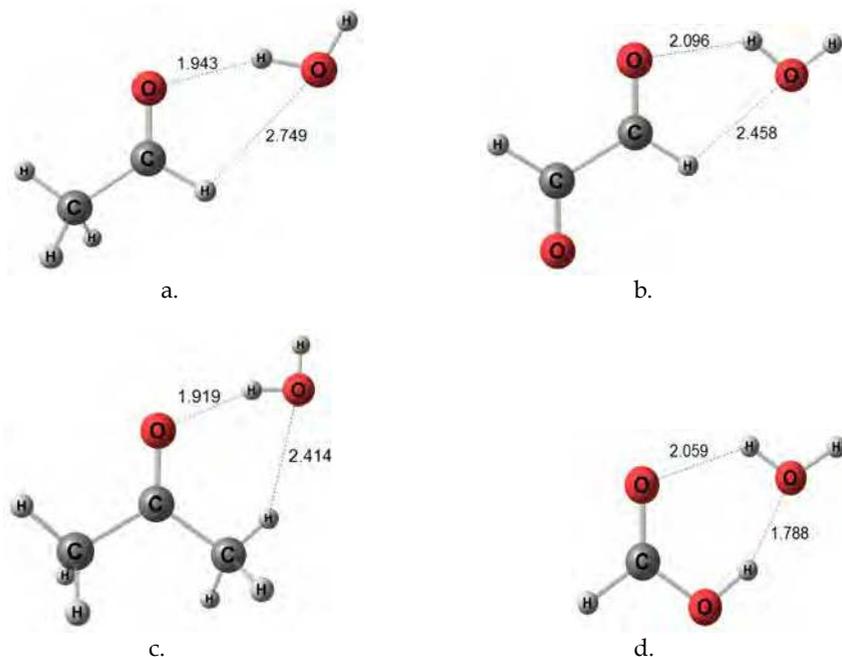
Fig. 5. Water complexes and percent of complex formed at 298K, with acetaldehyde, glyoxal, acetone and formic acid.

strong H bonds between water, a polar molecule and the free radical. Some of these complexes are shown in Fig. 6 and relevant distances are given in Å.

The concentration of atmospheric water, although variable, is always in large excess with respect to both OH and COV's. This, together with the fact that, in the above mechanism, water is a catalyst and therefore regenerates, allows us to use fixed water concentrations to obtain pseudo second order rate constants that depend parametrically on water concentration. Thus, the rate constant should be calculated as:

$$k = \sigma \, K_{eq0} \, K_{eq1} \, k_2 \, \kappa_2 \, [water]$$

where K_{eq0} and K_{eq1} are the equilibrium constants for Steps 0 and 1 respectively, k_2 and κ_2 are the unimolecular rate constant and the tunneling factor for Step 2, and σ is the reaction symmetry number.

An alternative (but exactly equivalent) way to interpret the pseudo second order rate constant is to multiply the second order rate constant of the water-VOC complex + OH reaction by the molar fraction (X) of VOC that is complexed: this fraction is simply K_{eq0} [water]. The latter approach has the advantage of allowing for a direct comparison between rate constants obtained with the present methodology and similar calculations in which Step 0 was ignored. In this approach, the rate constant is then simply obtained as:

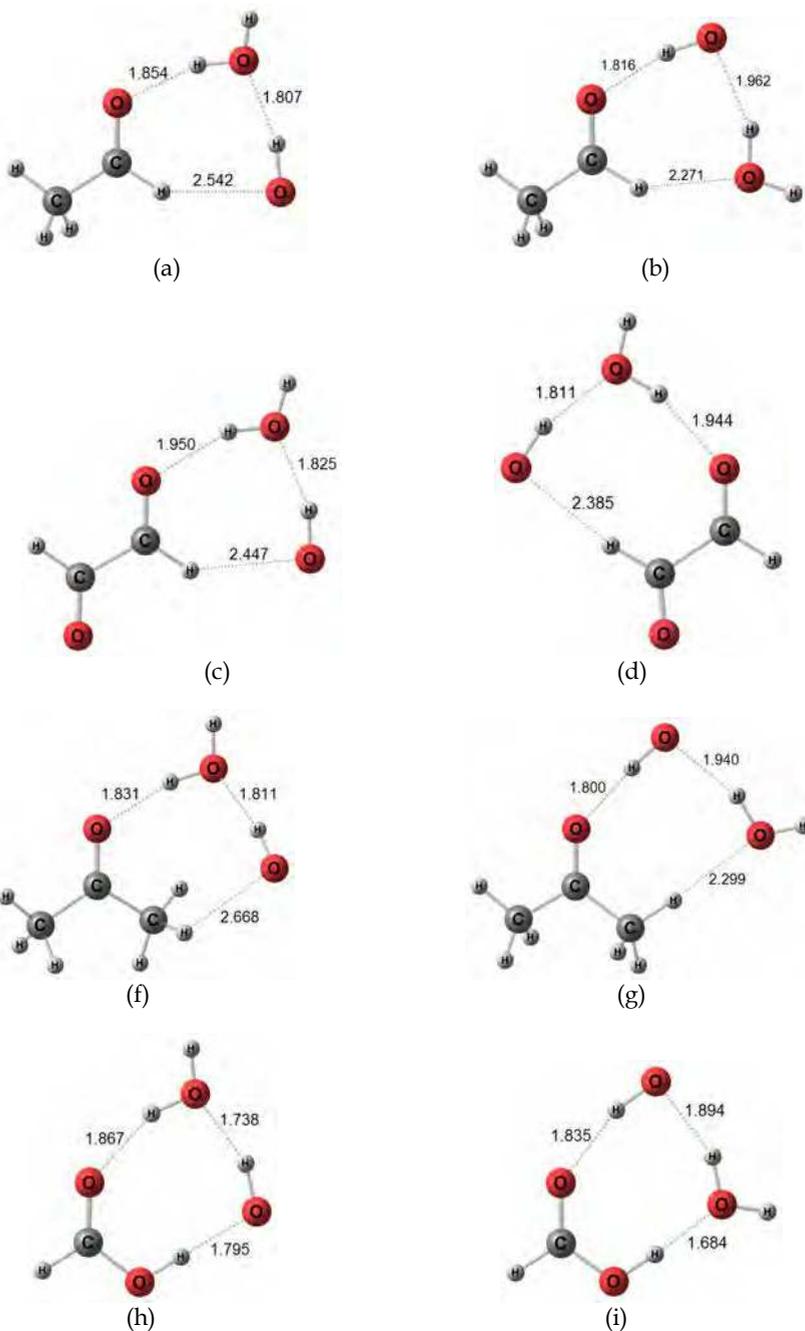$$k(\text{overall}) = (1 - X) \, k(\text{VOC}) + X \, k(\text{VOC-water complex})$$

Fig. 6. Termolecular pre-reactive complexes for acetaldehyde, glyoxal, acetone and formic acid.

In Table 1, we have collected the results for acetaldehyde, glyoxal, acetone and formic acid, at 298K. The calculated percent amount of complexed VOC is reported in the second column. Rate constants for the VOC + OH reaction in the absence of water are given in the third column, those for the complex are shown in the fourth column, and the overall result is reported in the last column.

VOC	% complex	k(VOC)	k(VOC-water) complex	k(overall)
acetaldehyde	0.01	1.58×10^{-11}	1.32×10^{-9}	1.58×10^{-11}
glyoxal	0.01	1.95×10^{-11}	4.25×10^{-10}	1.95×10^{-11}
acetone	0.02	1.04×10^{-13}	3.29×10^{-12}	1.04×10^{-13}
formic acid	12.0	4.39×10^{-13}	1.48×10^{-13}	4.04×10^{-13}

Table 1. Calculated percent amount of complexed VOC and rate constants at 298K.

It is interesting to discuss the specific reaction mechanism of each of the studied VOC individually, both in the presence and in the absence of water.

Reaction of acetaldehyde with OH occurs mainly by abstraction of the formyl hydrogen atom. Although the rate constant for the complex is several orders of magnitude larger than in the absence of water, the amount of complex formed is so small that the overall rate constant is practically unaffected even in a troposphere with 100% humidity (water concentration of 7.95×10^{17} molecules cm^{-3}, at 298.15 K). The variation with temperature was also analyzed. Slight changes are noticeable only below 220 K, i. e. at temperatures that are unattainable under usual atmospheric conditions. The experiment of Vöhringer-Martinez et al. was performed under severe laboratory conditions, and a large acceleration was observed at very low temperatures (50 K).

The reaction of free glyoxal with OH occurs by H-abstraction. When a water complex is formed, one of the formyl hydrogen atoms binds to water while the other one is still available for abstraction. Reaction of the glyoxal-water complex with OH is about 27 times faster than the corresponding reaction for free glyoxal + OH. However, the amount of water complex formed is less than 0.01%, and a reaction rate enhancement by single-water-molecule catalysis does not occur.

Reaction of both free and water-complexed acetone with OH occurs by hydrogen abstraction from a methyl group. Again, the amount of complex formed is only about 0.02 % at 298 K, and although the step 2 barrier is considerably lowered in the presence of a water molecule, no observable rate increase is expected.

The case of formic acid with OH is different than the preceding ones in the sense that the amount of water complex formed is small but relevant under atmospheric conditions (about 12% at 298 K), and it could in principle be large enough to produce a measurable increase in the overall rate constant. However, in the presence of water, the reaction mechanism is different from the one in a dry atmosphere. While in the water-free case the favored path is a PCET carboxylic hydrogen abstraction, in the water-assisted reaction the carboxylic hydrogen is strongly involved in the formic acid-water complex and it is therefore less available for reaction with an OH radical. Free energy values point to a preference for a

formyl hydrogen abstraction channel, which is considerably slower. Thus, once more, no single-water-molecule catalysis is observed.

In conclusion, it is safe to state that one water molecule *does not* accelerate the reaction of OH radicals with most volatile organic compounds under atmospheric conditions. The apparent rate coefficient taking into account atmospheric water concentration is considerably smaller than the one in the absence of water, independently of the method of calculation. The apparent disagreement between the present results and the experimentally observed rate coefficients in Vöhringer-Martinez et al. could be due to a possible catalytic effect of water molecules associations or because the experimental conditions do not match the atmospheric ones. Such reactions may still occur in molecular complexes consisting of several water molecules. These molecular complexes are known to be abundant prior to atmospheric aerosol nucleation events (Zhang et al., 2002), and have been shown to catalyze organic (including glyoxal) reactions in nanoparticles (Zhao et al., 2009; Wang et al., 2010). The study of these very interesting reactions is, however, outside of the scope of the present work.

5. Adsorption and reactivity of vocs on a mineral aerosol surface

Clay particles are present in large quantities in mineral dust in atmospheric aerosols and their interaction with organic species may, in principle, influence atmospheric reactions and the prediction of environmental risks. Thus, it is interesting to study the kinetics and mechanisms of adsorption and reaction of atmospheric volatile organic compounds bound to a model clay surface in order to understand and describe, at the molecular level, its effect on the reaction.

In this section, mechanistic and kinetic data for OH-initiated oxidation reactions of VOC's adsorbed on mineral aerosols models are discussed.

The rigid tetrahedron SiO_4 is the building block of all siliceous materials, from zeolites to quartz and amorphous silica. Clay minerals, or phyllosilicates, are formed by sheets of SiO_4 tetrahedrons joined to a sheet of Al oxide octahedrons (Figure 1). The ideal surface of a phyllosilicate is characterized by the presence of a large number of siloxane Si-O-Si bridges, forming hexagonal rings. However, a natural clay surface presents many structural defects and fractures, and its chemical properties are largely due to the presence of active sites on the surface. These are mainly acid sites (Brönsted sites, associated to aluminol and silanol groups) and Lewis sites (such as in four-coordinated Al phyllosilicates) that have large specific surfaces and catalytic properties. Therefore, their presence in aerosols can be expected to play an important role in the heterogeneous chemistry of the troposphere.

Within the quantum mechanical methodology, small clusters of silicate groups are used to model silicate surfaces (Sauer et al., 1994). The basic premise behind the cluster models is that reactions and adsorption are local phenomena that are primarily affected by the nearby surface structure. The active site is described explicitly by the interactions between the local molecular orbitals of the adsorbate and the adsorbent. Clearly, this methodology has the disadvantage that the electronic system is represented only partially, due to the small size and the discrete nature of the cluster employed. However, it has been shown to be adequate to represent a mineral aerosol surface and to allow the use of high accuracy quantum methods to describe the energetics of adsorption, reaction paths, and intermediates formation.

On the natural clay surface, silanol groups are the most reactive sites for adsorption of organic molecules and for their reactivity. Orthosilicic acid $Si(OH)_4$ has been validated as a good model for both isolated and geminal silanol hydroxyl groups and we have used it to mimic the OH reaction with formaldehyde and formic acid on a silicate surface (Iuga et al., 2008a). Vicinal silanol groups may be studied by means of the $(HO)_3Si-O-Si(OH)_3$ dimer. In this model, substitution of a Si cation by a tetrahedral Al is useful to represent a wide range of silicates with Lewis or Brönsted acid properties. The silicate hexagonal six-member ring characteristic of a clay surface may be studied by means of a cyclic hexamer model, with and without an OH surface group. In Figure 7 we show the silicate models employed.

The adsorption energy is defined as the difference between the total electronic energy of the surface-adsorbate complex and the sum of those of the isolated molecule and the model surface, including ZPE corrections:

$$\Delta E_{\text{adsorption}} = E_{\text{adsorption complex}} - (E_{\text{molecule}} + E_{\text{surface}}) + \Delta(ZPE)$$
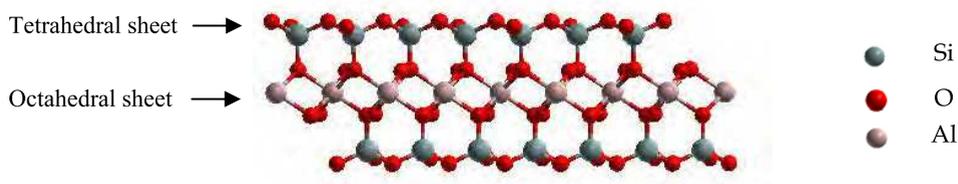
a) TOT silicate sheet.
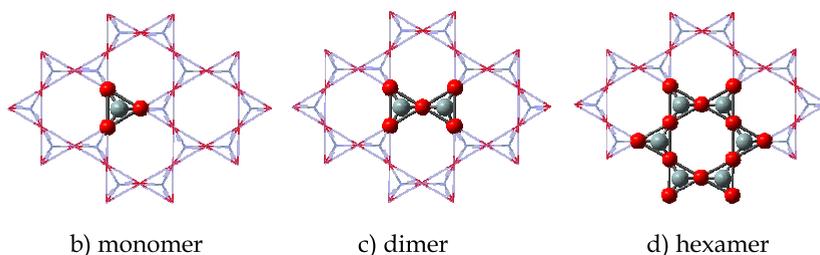
b) monomer   c) dimer   d) hexamer

Fig. 7. Silicate cluster models.

The most stable adsorption complex in the reaction of OH· radicals with formaldehyde adsorbed on an $Si(OH)_4$ monomer is shown in Fig. 8. In this complex, the formaldehyde molecule is clearly oriented perpendicularly to the surface and it attaches to the model surface by two hydrogen bonds. Surface hydroxyls play the role of a weak hydrogen donor and the adsorbed molecule assumes the role of the base.

The vibrational properties of silanol groups can be easily studied by infrared spectroscopy. On highly dehydrated surfaces, a single, well-defined band due to the OH stretch is measured at about 3742 cm^{-1} on an otherwise featureless spectral region extending from 3730 to 2000 cm^{-1}. It is then easy to study the perturbations of the OH stretching frequency upon adsorption of molecules from the gas phase. As an example, the formaldehyde

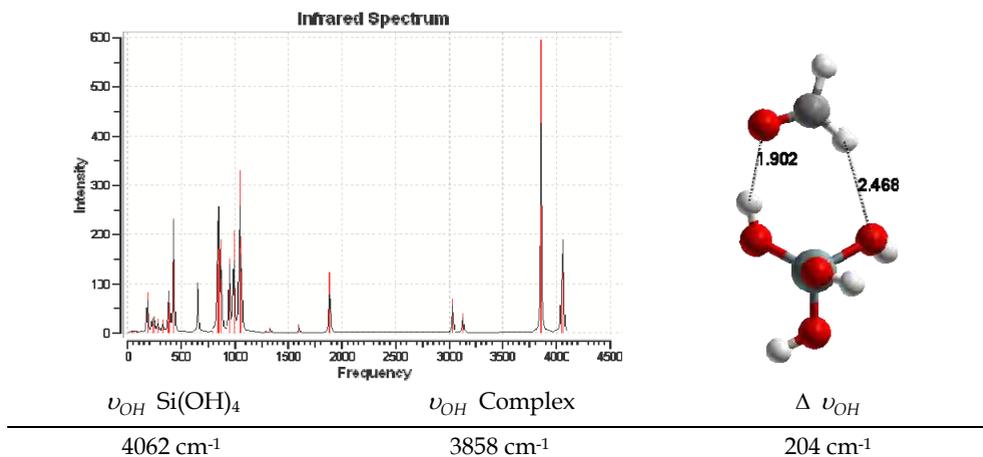| υ_{OH} Si(OH)$_4$	υ_{OH} Complex	$\Delta\ \upsilon_{OH}$
4062 cm^{-1}	3858 cm^{-1}	204 cm^{-1}

Fig. 8. Adsorption complex calculated infrared spectrum.

adsorption complex calculated infrared spectrum is shown in Fig. 8. The observed shift in the frequency of the O-H stretching involved in the main interaction is 204 cm^{-1}.

In the main reaction channel, formaldehyde reacts with OH radicals by hydrogen abstraction, to form a water molecule and a bound formyl radical. We showed that the rate constant for the H-abstraction reaction is an order of magnitude smaller when formaldehyde is bound to Si(OH)$_4$ than in the gas phase. Thus, on the basis of the calculated rate constants one can conclude that, when the OH-formaldehyde reaction occurs in the presence of dust, at atmospheric pressure, it is *slower*, by a factor of about ten, than the reaction in the gas phase. If one takes into account the fact that silicate aerosols are known to trap some of the OH radicals in the troposphere, the resulting decrease in the formaldehyde reaction rate with OH could be significant.

On a perfect silicate surface with no defects, there are no OH groups and adsorption is much weaker. This case can be modelled with a simple hexamer with no OH groups on the surface, as shown in Figure 9.

Results obtained for the formaldehyde + OH reaction using larger cluster models (Iuga et al., 2008b) with OH groups on the surface yield results that are equivalent to those of the Si(OH)$_4$ model and suggest that, at least for small molecules, the monomer model is sufficient to qualitatively predict the main effects of mineral aerosols.

Adsorption of larger (C2-C5) aliphatic aldehydes on silicate clusters active sites, and their subsequent reaction with OH radicals was also studied (Iuga et al. 2010). Different adsorption complexes were found, and it is clear that the adsorption complex structure determines the subsequent path of its reaction with OH. The initial step in the OH reaction with acetaldehyde occurs according to the same mechanism as in the gas phase, i.e., the aldehydic hydrogen abstraction. Starting from propanal, another abstraction channel becomes increasingly important, involving mainly the abstraction of a hydrogen of the aliphatic chain. In the presence of a silica monomer model surface, the reaction rate of acetaldehyde with OH is found to be about one seventh its value in the gas phase. Because
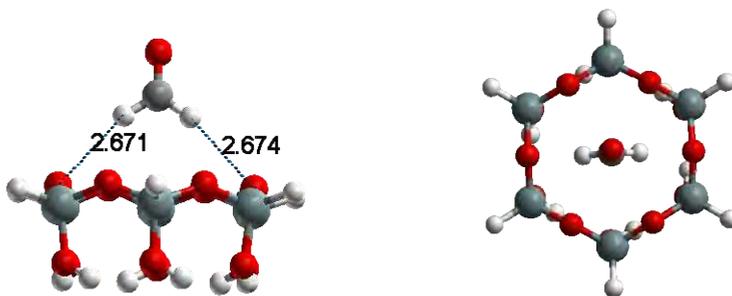
E_{ADS} = 3.05 kcal/mol

Fig. 9. Formaldehyde adsorbed complex.

of the abundance of this contaminant, our results may have implications in tropospheric chemistry. For larger aldehydes, the rate constant is also consistently smaller than in the gas phase. Results are summarized in Table 2.

VOC	*Alkyl H-abstraction*		*Aldehydic H-abstraction*		$k^{overalll}$ (x 10^{-11})	$k^{experimental}$ (x 10^{-11})
	k^{eff} (x 10^{-11})	%	k^{eff} (x 10^{-11})	%		
Acetaldehyde	0.0068	3.00	0.22	97.00	0.23	1.50, 1.50, 1.44
Propanal	0.30	42.86	0.40	57.14	0.70	1.90, 2.06, 1.99
Butanal	1.37	65.87	0.71	34.13	2.08	2.88, 2.38, 2.38
Pentanal	0.38	35.18	0.70	64.82	1.08	2.48, 2.61, 2.76

NIST data base (http://kinetics.nist.gov/kinetics/index.jsp).

Table 2. Calculated total rate constants (in cm^3 molecule^{-1} s^{-1}) and branching ratios at 298 K, for OH H-abstraction reactions of C2-C5 aldehydes on the $Si(OH)_4$ model. Experimental values correspond to the gas phase reaction have been taken from the NIST data base.

Adsorption of other contaminants, such as carboxylic acids and several polyaromatic heterocycles have also been studied on silicate model clusters. In general, these compounds use their most reactive groups to add on the silanol groups, and consequently their OH reactivity is smaller than in the gas phase.

6. Conclusions

In this article, we have reviewed our work on the mechanisms and kinetics of selected VOCs towards OH free radicals.

Quantum chemistry and computational kinetics methods have been used to model mechanisms and kinetics of the reactions of OH radicals with several groups of organic compounds (alkanes, alkenes, dienes, aromatics, aldehydes, carboxylic acids, alcohols, ethers, etc.) under tropospheric conditions. We have calculated reaction profiles, rate constants and branching ratios for numerous volatile organic compounds with OH and other radicals. Insight into reactivity trends, both in the gas phase and in the presence of mineral aerosol

models has been obtained. The relative site reactivity of the studied compounds towards OH radicals has been shown to be strongly influenced by intramolecular hydrogen-bond-like interactions that arise in the transition states. The usefulness of quantum chemical calculations to elucidate the detailed mechanisms of OH radical reactions with oxygenated VOCs has been proven. We show that the theoretical methodology employed provides accurate kinetic data that reproduce well the available experimental results and provide new data for a large number of troposheric reactions. Although the calculations performed in the references cover a list of different quantum chemistry methods that have been used over the years, our latest work has been performed using the M05-2X density functional method developed specifically for kinetic studies by the Truhlar group.

The correct explanation of the anti-Arrhenius behavior common to many radical-molecule reactions has been elucidated. The importance of including reactant complexes in the modeling in order to obtain accurate values of the rate coefficients, has been shown. The best results are those obtained when it is assumed that such complexes are in their vibrational ground state.

The possibility of one-water-molecule catalysis in OH reactions with volatile organic compounds is discussed, and it is shown that it does not occur.

Since the main daytime troposheric sink of oxygenated VOCs is their reactions with OH radicals, the mechanistic and kinetic information discussed in this work is essential in order to fully understand their troposheric chemistry as well as their subsequent fate. Hopefully, the large amount of experimental and theoretical work that has been revisited here, which has been devoted to chemical reactions of environmental significance, could contribute in some extent to act in the right direction and prevent more damage to the atmosphere.

7. Acknowledgment

8. References

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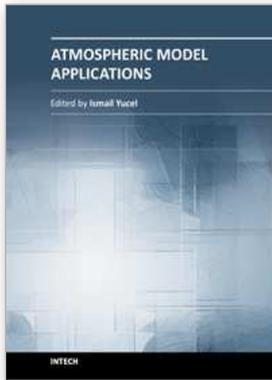
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