Theoretical Study of the Reaction between OH Radicals and Formaldehyde adsorbed on Small Silica Clusters

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ABSTRACT

Heterogeneous reactions of atmospheric gases on aerosol particles may play an important role in atmospheric chemistry. However, the kinetics and mechanisms of adsorption and reaction of atmospheric gases on aerosol surfaces are not well understood. Clay particles are present in mineral dust in atmospheric aerosols, and radical reactions are thought to be heterogeneously catalyzed on them. In this work, quantum chemical methods are used to study the reaction of OH radicals with formaldehyde adsorbed on small $(SiO_4)n$ cluster models. We show that surface adsorbed formaldehyde can react in the presence of gas phase OH radicals to yield surface-bound formyl radicals and water. With the models employed, the reaction appears to be more favored on the silicate surfaces than in the gas phase. The effect of the model surface on the reaction mechanism is analyzed.

Keywords: atmospheric chemistry, mineral dust, pollutants, troposphere, OH radicals, formaldehyde, phyllosilicates, aerosols, reaction mechanism, small clusters.

1. INTRODUCTION

A major natural component of atmospheric aerosol is mineral dust, which enters the atmosphere from dust storms in arid and semiarid regions. About 33% of the earth's land surface is arid and a potential source region for this atmospheric mineral aerosol.

Mineral aerosol is a general expression for fine particles of crustal origin that are generated by wind erosion, and which consist mostly of silica and silicate minerals. Particles smaller than 10 μm have week-long atmospheric lifetimes [1] and they may be transported over thousands of kilometers. The transatlantic transport of Saharan dust to North America is a well-studied phenomenon (see reviews [1], [2] and recent articles [3], [4]).

The chemical and mineralogical composition of mineral aerosol is complex [5]. Globally, the most important minerals of the clay fraction ($< 2 \mu$m) transported in dust storms are illite, kaolinite, chlorite, and montmorillonite/smectite [6] whereas coarser particles mainly consist of quartz, feldspars, and carbonates [7]. Dust aerosols in the lower stratosphere consist almost entirely of clay particles [8].

Clay minerals, or phyllosilicates, are formed by sheets of SiO_4 tetrahedrons joined to a sheet of Al oxide octahedrons. The great diversity of these layered silicates is due to their capability for isomorphous substitution of various cations in the octahedral and tetrahedral sheets. Phyllosilicates 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.

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. Laboratory studies, together with field observations and modeling calculations, have clearly demonstrated the importance of heterogeneous processes in the atmosphere. Some works have tried to quantify the effect of dust on tropospheric chemistry: Dentener et al. [1996] concentrated on heterogeneous uptake. He calculated that ozone concentration would decrease both because O_3 production decreased (N_2O_5 and HO_2 were taken up on dust) and because the O_3 molecules were themselves taken up on dust. Bian and Zender [2003] quantified the effect of dust on tropospheric chemistry due to both photolysis and heterogeneous update. They found that on a global average, O_3 decreases by 0.7%, OH decreases by 11.1%, and HO_2 decreases by 3.5 % when dust is added to the atmosphere. As discussed by Ravishankara, the ability to accurately predict the composition of the troposphere will depend on advances in understanding the role of particulate matter in the atmosphere and the extent to which heterogeneous reactions on solids and multiphase reactions in liquid droplets contribute to the chemistry.

The primordial role of OH radicals in the oxidative transformation of volatile organic compounds and other pollutants in the troposphere has stimulated interest in the study of their atmospheric reactions. Both experimental and theoretical studies of atmospheric reactions with OH radicals in the gas phase have been reported for a large number of reactions [9], [10], [11], [12], [13]. In most cases, these reactions are very fast, and accordingly, OH is the main oxidant of volatile organic species in the troposphere. However, the catalytic loss processes of atmospheric pollutants in the presence of OH radicals are not clear. Aerosols may promote the chemical reactions of OH radicals with adsorbed pollutants [14], [15].

Formaldehyde is an important component of the polluted troposphere. Concentrations of CH_2O measured in the remote troposphere are often lower and show considerably more variability than values computed from standard photochemical models [16], [17], [18], [19]. Some model studies have proposed that heterogeneous chemistry in aerosols and clouds could provide a fast sink for CH_2O [20], [21] though field observations offer no support for this hypothesis. Measurements of CH_2O gas-aerosol partitioning in surface air [22] indicate that only a small fraction of CH_2O is present in the aerosol. Observations in fogs and clouds show no evidence of CH_2O depletion relative to clear sky [23], [24], [25]. As formaldehyde is an important precursor to HOx in the troposphere, any heterogeneous interactions it may have with aerosol could potentially affect HOx levels, especially if it is removed from the troposphere. In a recent study by Carlos-Cuellar *et al.* examining the reaction of formaldehyde on SiO_2, [26] they found that the reaction of formaldehyde on SiO_2 are reversible.

Formaldehyde may, in principle, react with an OH radical according to two reaction paths: the abstraction of a hydrogen atom and the subsequent formation of a water molecule and a formyl radical; or, addition of the OH radical to the double bond, with the formation of the $H_2C(OH)O\bullet$ alkoxy radical. In the gas phase at room temperature, the abstraction reaction is favoured. The experimentally determined Arrhenius parameters [27], [28] indicate that the activation energy barrier is negative and very small. The gas phase formaldehyde + OH reaction has been studied by Galano *et al.* [12] who showed that a complex mechanism, involving the formation of a pre-reactive complex, explains adequately the observed negative activation energy of the reaction and the preference for the abstraction path. However, if the formaldehyde molecule were anchored to a clay surface, the branching ratio between the two reaction paths could be significantly altered.

Theoretical studies on clusters or molecular models of silicates have been performed by several authors, many of them concerning models for zeolites [29], [30], [32]. Sauer and co-workers have made an exhaustive revision of quantum mechanical models used to study molecule-solid interactions [31]. These methods have been shown to provide useful results for local properties of solids. Molecular Van der Waals complexes between adsorbed molecules and surfaces have been studied [32] and adsorption energies have been reproduced for a large number of compounds. The adsorption of methanol, formaldehyde and formic acid on hydrohylated silica surface has been studied [33] using DFT methods and ONIOM calculations on small clusters. To the best of our knowledge, there has been no report of a radical-molecule reaction mechanism study being performed for a molecule adsorbed on a surface.

The cluster model has been widely used to represent the active sites of solid catalysts, because it allows the performance of full geometry optimizations of minima and transition states as well as frequency calculations with high quality quantum chemical methods. However, it has some disadvantages, such as the appearance of boundary effects where the cluster is separated from the crystal framework, or the neglect of the long-range electrostatic effects caused by the Madelung potential of the solid.

The rigid tetrahedron SiO_4 is the building block of all siliceous materials, from zeolites to quartz and amorphous silica. At the surface, the structures terminate either in a siloxane group with oxygen on the surface, or in isolated, vicinal or geminal silanols [34], [35], [36].

The easiest and chemically best defined procedure for making a cluster neutral is to saturate the dangling bonds resulting from a homolytic cut with monovalent atoms, normally hydrogen [37]. Different small clusters have been used in the literature to model silicate surfaces [38], [39].
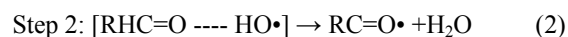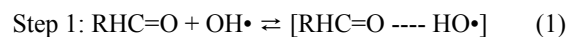
In this work, the mechanism of the formaldehyde + OH hydrogen abstraction reaction will be studied, with the formaldehyde attached to a model silicate cluster. It is clear that the results will depend significantly on the choice of the cluster model. As a first tentative approach, simple monomer, dimer and trimer clusters will be used. Our aim is to identify a computational method and a cluster size and geometry that is adequate to yield reliable results for this type of reactions.

2. METHODOLOGY

In order to study the reaction of an OH radical with a volatile organic compound adsorbed on the surface of a mineral dust aerosol model, we have chosen the reaction of a formaldehyde molecule with an OH radical. On the one hand, formaldehyde is a very reactive polar molecule that is easily adsorbed on surfaces, and on the other hand, many theoretical and experimental data are available for this gas phase reaction.

At first, different cluster surfaces have been modeled using several quantum chemistry methods. Then, formaldehyde is adsorbed on the surface, and an OH radical is allowed to approach the adsorbed formaldehyde. In this work, the BH&HLYP/6-311G** method was chosen. The gas phase reaction of formaldehyde with an OH radical was calculated at this level. Reactants, the pre-reactive complex, the transition state and the final intermediate product were optimized at this level of theory. The corresponding energy profile and optimized structures are shown in Figure 1.

In this mechanism, the reaction occurs in two steps: at first, a fast pre-equilibrium between the reactants and the pre-reactive complex is established, followed by an internal rearrangement leading to the elimination of a water molecule:

Step 1: RHC=O + OH$\bullet$ $\rightleftharpoons$ [RHC=O ---- HO$\bullet$]   (1)

Step 2: [RHC=O ---- HO$\bullet$] $\rightarrow$ RC=O$\bullet$ +H_2O (2)

The calculated structures are similar to the ones previously found theoretically by Alvarez Idaboy et al [12]. The calculated activation energy barrier al BHandHLYP/6-311g** level is 0.23 kcal/mol, very close to the experimental results, which vary between +0.4 and -0.4 kcal/mol [40].
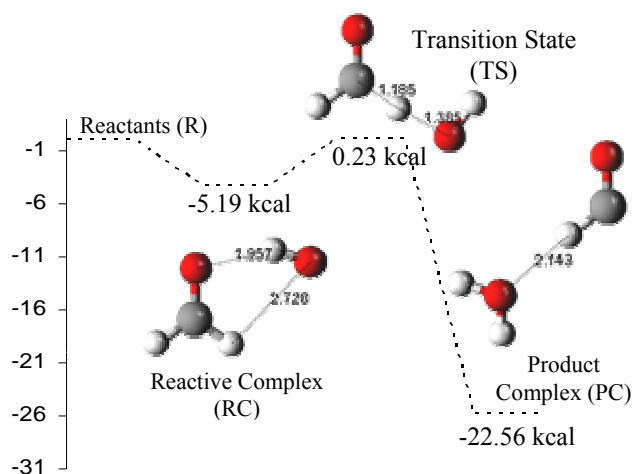

Figure 1: Gas phase reaction energy profile.

The surface models have to represent the structural features of the system simulated as closely as possible, but they have to be limited in size. In this work, three surface models have been considered, corresponding to the monomer, the dimer and the trimer.

Standard ab initio quantum chemical calculations were performed using the standard density functional BHandHLYP method as implemented in the Gaussian 03 program package. All geometries were fully optimized at this level using the Berny analytical gradient method. The unrestricted approximation was used for radicals. Normal mode analyses were carried out at the same level to confirm the nature of the various stationary points, only positive eigenvalues for minima and one negative eigenvalue (imaginary frequency) for transition states. The motion along the reaction coordinate corresponds to the expected transition vector. Corrections for zero-point energy (ZPE) (vibrational energy at 0ºK) were taken from the force constant analysis and added to the total energies.

3. RESULTS AND DISCUSSION

The optimized cluster geometries are shown in Figure 2 In all cases, full geometry optimization was achieved. It can be observed that for all surface models, the Si-O distance varies between 1.61Å and 1.64Å, and the O-H distance is about 0.95 Å, both in very good agreement with the experimental data for clay minerals. The O-Si-O angle varies between 102.9 and 115.7.

The initial step starts with the adsorption of a formaldehyde molecule. In all cases, the formaldehyde molecule is adsorbed on the model surface in a plane that is perpendicular to the surface. A weak adsorption complex is formed. When OH dangling bonds are available, one of the formaldehyde H atoms is oriented towards the surface O atoms while its oxygen atom is attracted to a surface terminal hydrogen. Both non-bonding H…O distances correspond to weak hydrogen bonds. In our calculations, the formaldehyde molecule is allowed to move freely until it reaches the optimum adsorption site. All surface-adsorbate complexes have been fully optimized at the BHandHLYP/6-311G** level. Figures 4.(a), 5.(a) and 6.(a) show the optimized geometry of formaldehyde adsorbed on the surface models considered in this work. Relevant bond lengths are indicated on the figures.

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

$$E_{adsorption} = E_{surface-adsorbate\ complex} - \\ -(E_{molecule} + E_{cluster}) + \Delta ZPE \qquad (3)$$

Adsorption energy results are summarized in Table 1. They are similar for all surface models, and they are negative, indicating that formation of the adsorption complex is exothermic.

The OH radical attack on adsorbed formaldehyde occurs in the following way. At first, the positively charged hydrogen atom of the OH radical approaches a lone pair of the oxygen atom to form a stable pre-reactive complex. In this complex, the OH radical lies in the plane of the CHO group (see figures 4.(b), 5.(b) and 6.(b)).

a). monomer $Si(OH)_4$ b). dimer $(H0)_3Si-O-Si(OH)_3$ c). trimer $(H0)_3Si-O-Si(OH)_2-O-Si(OH)_3$
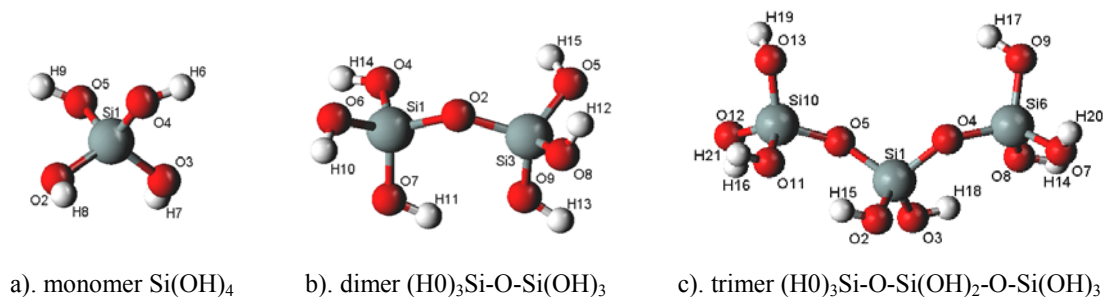
Figure 2: BHandHLYP/6-311G** cluster models.

Prereactive complexes seem to be common in all radical-molecule reactions, and they are due mainly to the long-range Coulombic interactions between the reactant molecules. The geometries of the pre-reactive complexes obtained for the reaction between OH radical and formaldehyde adsorbed on the surfaces are very similar in all cases and very close to those obtained in the gas phase. Concerning the stabilization energy of the pre-reactive complexes (which is equal to E_{-1}), the results obtained with the three different surface models employed range from 3.18 kcal/mol to 5.19 kcal/mol.

From this structure, the oxygen of OH may flip, in the plane, toward the hydrogen to be abstracted as the energy increases to a maximum at the transition state. The transition state for this reaction step has been identified, and the vibrational motion associated with the imaginary frequency shows that the reaction involves an H atom migration. Calculated transition state energies are lower (for the dimer and trimer models) or slightly higher (in the case of the monomer) than the energy of the reactants, thus yielding an effective negative activation energy for the reaction. Thus the larger models predict that reaction is considerably faster on the surface than in the gas phase.

However, concerning the heats of reaction (Table 1), the employed method predicts the reaction path to be less exothermic than in the gas phase.

The energy profile of the reaction is shown in Figure 3. The stabilization energy of the prereactive complexes (E_{-1}), the effective activation energies $E_a^{eff} = E_2 - E_{-1}$ at 0 K, and the heat of reaction $\Delta H = E_P - E_R$ at 298 K, of the adsorbed formaldehyde + OH reaction are given in Table 1. The ZPE corrections have been included in all the energy differences.
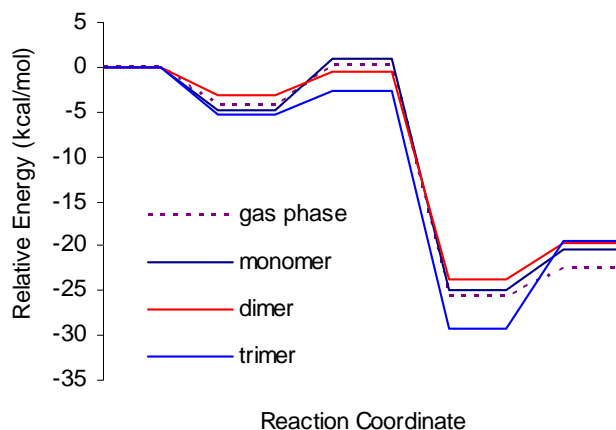

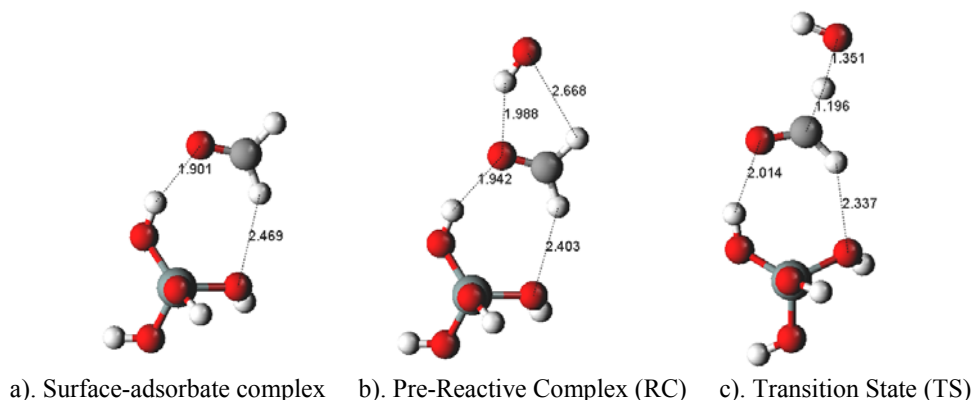Figure 3: Reaction energy profile.

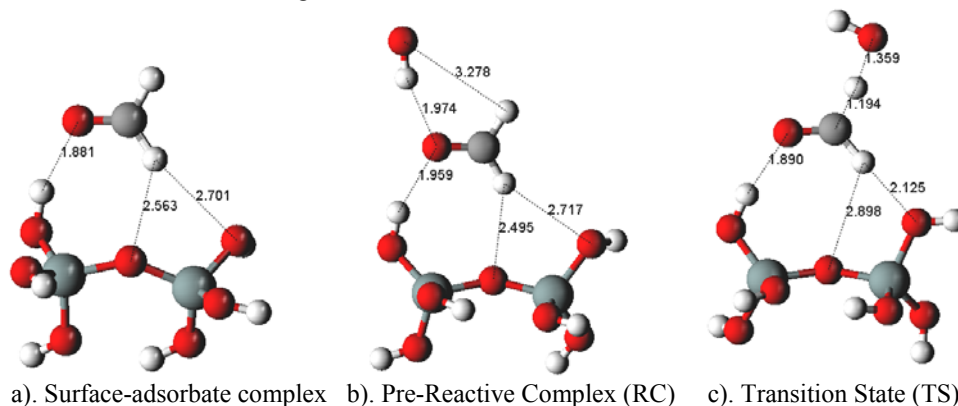a). Surface-adsorbate complex   b). Pre-Reactive Complex (RC)   c). Transition State (TS)

Figure 4: Reaction on monomer surface.

a). Surface-adsorbate complex   b). Pre-Reactive Complex (RC)   c). Transition State (TS)

Figure 5 : Reaction on dimer surface

a). Surface-adsorbate complex.

b). Pre-Reactive Complex (RC).

c). Transition State (TS).
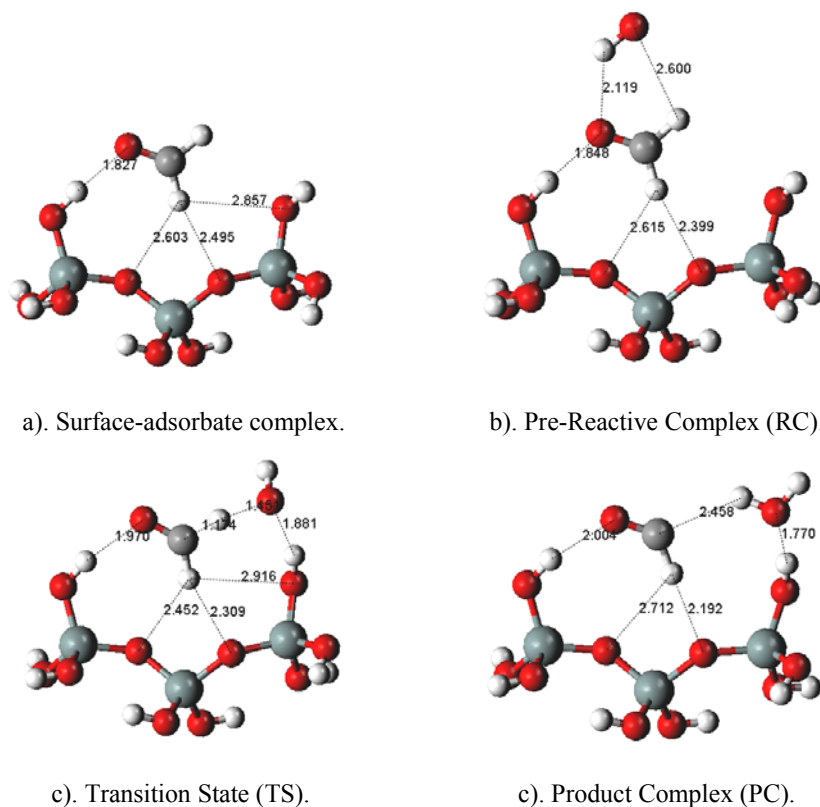
c). Product Complex (PC).

Figure 6: Reaction on trimer surface**.**

Table 1.- BHandHLYP/6-311g** relative barrier energies (including the ZPE corrections) and Heat of Reaction Energies (ΔH), in kcal/mol, of the OH radical reaction with formaldehyde adsorbed on different surface models (in kcal/mol).

Surface model	$E_{adsorption}$	E_{-1}	E_2	E_a^{eff}	ΔH	Imaginary frequency (cm^{-1})
gas phase	-	-5.19	5.42	0.23	-22.56	-932
monomer	-6.38	-4.92	5.83	0.92	-20.35	-1,204
dimer	-7.77	-3.18	2.59	-0.59	-19.68	-1,147
trimer	-9.14	-4.99	2.23	-2.76	-29.19	-659

$$E_{-1} = E_{stabilization} = E_{RC} - E_R$$

$$E_2 = E_{TS} - E_{RC}$$

$$E_a^{eff} = E_{TS} - E_R$$

$$\Delta H = E_P - E_R$$

3. CONCLUSION

In this work, the mechanism of the formaldehyde + OH hydrogen abstraction reaction have been studied, with the formaldehyde attached to a model silicate cluster. We have shown that, if small cluster models are used to represent SiO$_2$ surfaces, the reaction of adsorbed formaldehyde with OH radicals yields surface-bound formyl radicals and water. The geometries of the equilibrium structures (surface-adsorbate complexes, pre-reactive complexes and transition states) are very similar in all cases and very close to those obtained in the gas phase.

The obtained results are compared with those available in the literature for the formaldehyde + OH radical reaction in the gas phase. The convergence of the results with increasing size of the surface model seems to indicate that the presence of the surface favors the reaction rate.

Extension of the present work in several directions (larger surface molecular models, periodic models, inclusion of thermodynamic data, consideration of the cavity structure) is both possible and necessary in the future, and it is being performed.

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