On the OH initiated oxidation of C2–C5 aliphatic aldehydes in the presence of mineral aerosols

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Abstract

Clay particles are present in large quantities in mineral dust of atmospheric aerosols, and their interaction with organic species may influence atmospheric reactions and the prediction of environmental risks. However, the kinetics and mechanisms of adsorption and reaction of atmospheric volatile organic compounds on aerosol surfaces are not well understood.

In this work, quantum chemical methods are used to study the adsorption of C2–C5 aliphatic aldehydes on silicate clusters active sites, and their subsequent reaction with OH radicals. It is shown that adsorption may occur in two different ways, and 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 β-hydrogen of the aliphatic chain. In the presence of a silica monomer model surface, the reaction rate of aldehydes with OH free-radicals is smaller than in the gas phase. Furthermore silicates are good sinks for trapping these aldehydes. Thus, our results may have implications in the study of tropospheric chemistry and cosmochemistry.

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1. INTRODUCTION

Aerosols impact the chemical composition of the atmosphere by providing a surface for heterogeneous chemistry, and for light scattering and absorption at photolytic wavelengths (Bian and Zender, 2003). In particular, mineral aerosols are fine particles of crustal origin that are generated by wind erosion, and that consist mostly of silica and silicate minerals. Although these dust particles are very abundant in the Earth’s atmosphere, comprising nearly 45% of global aerosol emissions, the role of mineral aerosols in atmospheric chemistry is currently not well understood, and in fact it is not known whether they will act as catalysts or if they will instead reduce the reaction rate.

Previous works have studied the effect of dust on tropospheric chemistry. Dentener et al. (1996) calculated that ozone concentration would decrease because O3 production decreased and also because the O3 molecules were themselves taken up on dust. Bian and Zender (2003) found a decrease in concentration of free-radicals when dust is added to the atmosphere. An accurate prediction of the tropospheric composition will depend on advances in understanding the role of particulate matter and the extent of heterogeneous reactions on solids as well as multiphase reactions in liquid droplets (Ravishankara, 1997). Thus, the heterogeneous chemistry of trace atmospheric gases on solid-phase particles in the troposphere is a field of great interest (Oh and Andino, 2002; Sørensen et al., 2002).

On the other hand, the oxidative transformation of volatile organic compounds in the troposphere is driven mainly by OH free-radicals. Among these, carbonyl compounds such as aliphatic aldehydes are important components of the polluted troposphere, with lifetimes typically...
less than 10 h. They are removed from the troposphere both by photolytic processes yielding radicals as primary products, and by chemical reactions with OH radicals during day-time and NO3 radicals at night-time. Similar aldehyde compounds have been detected in interplanetary space, and silicates have also been detected in the galactic dust (Widicus Weaver and Blake, 2005). Therefore, the study of radical reactions with aldehydes on the surface of silicates will be interesting also for a better understanding of intergalactic cosmochemical reactions.

The gas phase aldehyde + OH reaction has been widely studied by experimental techniques (Butkovskaya and Setter, 1998; Atkinson, 2000) as well as by theoretical methods (Francisco, 1992; Alvarez-Idaboy et al., 2001). The available kinetic and mechanistic data show that the reaction of OH radicals with small aldehydes proceeds predominantly by overall H atom abstraction from the –CHO group to form an acyl radical and water. In general, hydrogen atom abstraction from the C=H bonds of the alkyl chain is considered to be of minor importance. The rate constants for these aldehydes fall in a small range between 1 and 3 × 10^{-11} cm^3 molecule^{-1} s^{-1} and increase slightly with the length of the alkyl group (DeMore et al., 1997; Atkinson et al., 2001; D’Anna et al., 2001). No theoretical mechanism and kinetics studies have been published for aldehydes larger than acetaldehyde.

In recent work, we have used quantum chemistry and computational kinetics to study the mechanism and kinetics of the reaction between OH radicals and formaldehyde adsorbed on small silica surface models (Iuga et al., 2008a, b) in order to estimate the possible effect of mineral aerosols on this reaction. Our results suggest that the rate constant for the H-abstraction reaction could be considerably reduced in the presence of these aerosols. 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 reactions rate constant with OH could have significant consequences in tropospheric chemistry.

In this work, the C2–C5 aliphatic aldehydes adsorption on the monomer model and their subsequent reaction with OH free-radicals is studied. Adsorption on a larger hexamer model will also be studied for comparison. All hydrogen abstraction channels will be considered. With the corresponding partition functions, the effective rate constants will then be calculated using classical Transition State Theory and the proposed mechanisms. The results will be compared with available experimental data in the gas phase. Our aim is to investigate the shape of the possible adsorption complexes and the effect that the presence of the orthosilicic acid and of the alkyl chain length has on the OH reaction mechanism, and to determine whether or not the adsorbed aldehydes react faster with OH radicals than when they are free.

2. COMPUTATIONAL METHODOLOGY

Electronic structure calculations have been performed with the Gaussian 03 program package (Frisch et al., 2004), using the DFT M05-2X functional (Zhao et al., 2006) that has been developed for accurate kinetic calculations. The reliability of DFT methods to describe properly chemical reactions has been discussed elsewhere (Ziegler, 1991; Siegbahn and Blomberg, 1999; Fernández-Ramos et al., 2006). The M05-2X functional has been parameterized to take into account dispersion forces as well as the basis set superposition error. 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 larger systems (Vega-Rodriguez and Alvarez-Idaboy, 2009). We have used the 6-311++G** basis set, which is known to yield a good description of hydrogen-bonded complexes and transition structures involving hydrogen transfer, such as those considered in this work.

Unrestricted calculations were used for open shell systems. Frequency calculations were performed for all the stationary points at the same level of theory as the geometry optimization and local minima and transition states were identified by the number of imaginary frequencies. It was verified that the atomic motion along the reaction coordinate corresponds to the expected transition vector. Corrections for zero-point energy (ZPE) (residual vibrational energy at 0 K) were obtained from the force constant analysis and were added to the total energies. Intrinsic Reaction Coordinate (IRC) (Gonzalez and Schlegel, 1990) calculations were also calculated to confirm that the transition states structures properly connect reactants and products.

Within the quantum-mechanical methodology, different small clusters have been used in the literature to model silicate surfaces (Sauer et al., 1994). The basic premise behind this approach is that reactions and adsorption are local phenomena that are primarily affected by the nearby surface structure. With this cluster approach, the active site is described explicitly by the interactions between the local molecular orbitals of the adsorbate and the adsorbent. Clearly, the corresponding 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, orthosilicic acid Si(OH)4 has been validated as a good model for both isolated and geminal silanol hydroxyl groups (Ugliengo et al., 1990; Civalleri et al., 1998; Pereira et al., 1999) and we have used it in our previous work to mimic a silicate surface on the OH reaction with formaldehyde (Iuga et al., 2008b).

The calculated rate constants were obtained using conventional Transition State Theory (CTST) (Eyring, 1935; Truhlar et al., 1983). Tunneling corrections were determined using the Eckart asymmetrical barrier as implemented in The Rate program at the Computational Science and Engineering Online website (www.cseo.net) (Zhang and Truong, 2001).

The proposed reaction mechanism is:

\begin{equation}
\text{Step 1: } RHC=O + OH_\bullet \xrightarrow{k_1} [RHC=O \cdots HO^-] \quad (1)
\end{equation}

\begin{equation}
\text{Step 2: } [RHC=O \cdots HO^-] \xrightarrow{k_2} \text{Products} \quad (2)
\end{equation}

This type of mechanism is well established for gas phase radical-molecule reactions. It was proposed by Singleton and Cvetanovic (1976), and it was used previously by us.
in quantum chemistry-TST calculations to study OH addition reactions to alkenes (Alvarez-Idaboy et al., 2000) and OH hydrogen abstractions in alkenes (Alvarez-Idaboy et al., 2001). The mechanism involves the formation of a pre-reactive complex that is in equilibrium with the separated reactants, followed by the irreversible formation of the products. According to this mechanism, if \( k_1 \) and \( k_{-1} \) are the forward and reverse rate constants for the first step and \( k_2 \) corresponds to the second step, a steady-state analysis leads to a rate coefficient for each overall reaction path that can be written as:

\[
k = \frac{k_1 k_2}{k_{-1} + k_2}
\]

(3)

Although the energy barrier for \( k_{-1} \) is in the same magnitude order that one for \( k_2 \), the entropy change is much larger in the reverse reaction than in the formation of products. Hence, following the hypothesis proposed by Singleton and Cvetanovic (1976), \( k_2 \) is expected to be much smaller than \( k_{-1} \). Based on this assumption, \( k \) can be rewritten as:

\[
k = \frac{k_1 k_2}{k_{-1}} = \left( \frac{A_1 A_2}{A_1} \right) \exp\left[ -(E_1 + E_2 - E_{-1})/RT \right]
\]

(4)

where \( E_1 \) and \( E_{-1} \) correspond to the energy barriers of the forward and reverse directions for the Step 1, respectively; \( E_2 \) is the barrier for Step 2, and the \( A 's \) are the partition functions. Since \( E_1 \) is zero, the apparent energy barrier for the overall reaction channel is:

\[
E_a = E_2 - E_{-1} = (E^{TS} - E^{RC}) - (E^{RC} - E^R) = E^{TS} - E^R
\]

(5)

where \( E^{TS} \), \( E^{RC} \) and \( E^R \) are the total energies of the transition state, the reactant complex and the reactants, respectively. Considering basic statistical thermodynamic principles, the equilibrium constant (\( k_2/k_{-1} \)) of the fast pre-equilibrium between the reactants and the reactant complex may be obtained as:

\[
K_{eq} = \frac{Q^{RC}}{Q^R} \exp\left[ \frac{E^{RC} - E^R}{RT} \right]
\]

(6)

where \( Q^{RC} \) and \( Q^R \) represent the partition functions of the reactant complex and the isolated reactants, respectively.

Under sufficiently high-pressure conditions, such as normal conditions in the troposphere, an equilibrium distribution of reactants is maintained and the CTST formula can be applied (Pilling and Seakins, 1996) to calculate \( k_2 \):

\[
k_2 = k_B T \frac{Q^{TS}}{Q^{RC}} \exp\left[ -\frac{E^{TS} - E^{RC}}{RT} \right]
\]

(7)

where \( k_B \) is the tunneling factor, \( k_B \) and \( h \) are the Boltzmann and Planck constants, respectively, and \( Q^{TS} \) is the partition function of the transition state. The energy differences include the ZPE corrections. The effective rate coefficient, \( k^{eff} \), of each channel is then obtained as:

\[
k^{eff} = \sigma K_{eq} k_2 = \sigma k_2 T \frac{Q^{TS}}{Q^R} \exp\left[ -\frac{E^{TS} - E^R}{RT} \right]
\]

(8)

where \( \sigma \) is the symmetry factor that is related to the reaction path degeneracy (Laidler, 1987).

3. RESULTS AND DISCUSSION

3.1. Adsorption complexes

In principle, when silanol groups are available on the silicate surface, an aliphatic aldehyde molecule binds rather strongly to a silanol hydrogen through its oxygen atom. In this work, we have chosen two silica cluster models: the Si(OH)\(_4\) monomer model and a cyclic hexamer model in which all but one of the surface silanol groups have been replaced by H atoms. The first one simulates vicinal silanol groups, while the second one mimics an isolated silanol active site.

The adsorption complexes were fully optimized. The potential energy surfaces were carefully spanned, and minima and maxima were evaluated. In this process, the aldehyde molecule was allowed to move freely until it reached the optimum adsorption site. The aldehyde approaches the surface model in two possible ways, and the most important interaction occurs always between the aldehydic oxygen and a silanol group. Additional weaker interactions involve hydrogen atoms in the aldehyde and other oxygen atoms on the surface. Two types of adsorption complexes are obtained for each model surface: ADS1 and ADS2. It is important to emphasize that, because the chains can adopt several geometries, scans were performed for the torsion angles of the aldehydes in order to insure that an absolute energy minimum conformer was obtained in each case.

The adsorption energy (Table 1) 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:

\[
E_{adsorption} = E_{adsorption complex} - (E_{molecule} + E_{surface}) + \Delta(E_{ZPE})
\]

(9)

In Fig. 1, both types of complexes have been represented for the C2–C5 aldehydes on the silicate monomer. In the ADS1 complexes, the aldehydic H interacts with a neighbouring oxygen atom, while the aliphatic chain extends away from the surface. In the ADS2 complexes, it is the chain hydrogen atoms that interact with the surface, as shown in Fig. 1. In the ADS1 complexes, the O\(_{ald}\)–H\(_{surf}\) distance is always about 1.82 Å, whereas in the ADS2 ones it is a little longer and in the range 1.84–1.87 Å. In ADS1 the H\(_{ald}\)–O\(_{surf}\) interaction distances are always about

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Hexamer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ADS1</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>−7.36</td>
</tr>
<tr>
<td>Propanal</td>
<td>−7.32</td>
</tr>
<tr>
<td>Butanal</td>
<td>−7.65</td>
</tr>
<tr>
<td>Pentanal</td>
<td>−7.57</td>
</tr>
</tbody>
</table>

Table 1 Adsorption energies (in kcal/mol) of the aldehydes on the silicate surface models (M05-2X/6-311++G**).
2.38 Å, while as in the ADS2 complexes, interactions between chain H atoms and surface oxygens occur at a much larger distance, that increases with the chain length. This implies that, for aldehydes with more than three carbon atoms, it is necessary to use a larger cluster model to account for these interactions.

If a larger surface model is used, as in the hexamer model, the longer chains have the possibility to establish more interactions with the surface (Fig. 2). The ADS1 type complexes are very similar to the ones previously described for the monomer. In the ADS2 complexes, except in the case of pentanal, they are also very similar, because the chains remain on one side of the hexamer and they interact only with the siloxane bridges that are close to the silanol active site. In pentanal, however, the aliphatic chain is almost long enough to cross the hexamer-ring, the molecule is adsorbed approximately in the middle of the ring, and it interacts with all of the siloxane bridges, thus increasing its adsorption energy.

In all cases, the adsorption energy values are negative, indicating that the adsorbates are stable and the silicates can be good sinks for trapping aldehydes. For the monomer model, the ADS1 adsorption energies are slightly larger than for the corresponding ADS2 structures. This can be explained because, in the ADS1 complexes, the adsorbate-surface interactions are stronger, with shorter H ... O distances than in the ADS2 ones. Nevertheless in the ADS2 complexes the number of the Halkyl ... Osurf interactions is bigger than in the ADS1 ones and the energy difference decreases when the alkyl chain length increases, because the number of Halkyl ... Osurf interactions increases.

On the contrary, in the case of the hexamer, the ADS2 adsorption energies are larger than the ADS1. The number of Halkyl ... Osurf interactions in the ADS2 complexes with the hexamer surface is larger than in the monomer surface model, because of the six surface siloxane oxygens. Hence, the adsorption energies for the ADS2 complexes increase with the length of the aliphatic chain.
3.2. Reaction mechanism

The next step is the approach of an OH free-radical to the adsorbed aldehyde molecule. It is mainly guided by the Coulomb interaction between the positively charged hydrogen atom of the OH radical and a lone electron pair on the aldehyde oxygen atom.

The use of the hexamer model to study this reaction is attractive, but it is prohibitive at this level of theory. However, in order to obtain accurate kinetic data, a high level of theory is necessary to calculate energies and partition functions. Thus, a pragmatic compromise must be achieved.

As shown in Figs. 1 and 2, the geometries for ADS1 and ADS2 complexes are very similar for the two surface models employed. In addition, adsorption energies for ADS1 complexes do not present a significant difference between the monomer and hexamer. Of course, a substantial increase in adsorption energies is observed in the case of ADS2 complexes when the larger model is used, due to the higher number of interactions between the chain and siloxane bridges. However, even in this case, the H atom that is free to be abstracted by the OH radical is out of the surface in both reaction channels, and we can hopefully assume that the increase in adsorption energy does not affect significantly the energy barrier of the reaction. Thus, for the above reasons, only the monomer model will be used in this work to study the reaction.

In principle, aliphatic aldehydes react with an OH radical through any one of three reaction paths:

(i) abstraction of the aldehydic hydrogen atom and subsequent formation of a water molecule and an acyl radical:

\[
\text{RCHO} + \cdot \text{OH} \rightarrow \text{RCO} \cdot + \text{H}_2\text{O} \quad (10)
\]

(ii) hydrogen atom abstraction from one of the alkyl chain C–H bonds:

\[
\text{RCHO} + \cdot \text{OH} \rightarrow \text{RCHO} + \text{H}_2\text{O} \quad (11)
\]

or

(iii) addition of an OH radical to the C=O double bond, with formation of the corresponding hydroxyl-acyl adduct radical:

\[
\text{RCHO} + \cdot \text{OH} \rightarrow \text{RCHO(OH)} \quad (12)
\]

Previous ab initio calculations for the gas phase reaction of the OH radical with formaldehyde and acetaldehyde indicate that the channel involving addition to the carbonyl group has a much higher activation energy than the elimination pathway (Aloisio and Francisco, 2000; Alvarez-Idaboy et al., 2001) and that its rate constant is about five orders of magnitude smaller (Alvarez-Idaboy et al., 2001). Thus, in these cases and in the gas phase at room temperature, the aldehydic H-abstraction channel is definitely favoured. The possibility that this branching ratio could change in the presence of a silicate surface was investigated in our previous work on formaldehyde + OH reaction.
(Iuga et al., 2008a), and it was shown that it was not significantly modified, the addition rate constant still being about a 1000 times smaller than the one for abstraction. In the present work, only abstraction pathways have been considered.

As in previous works on the adsorbed formaldehyde oxidation by OH radicals, the following reaction will be considered:

\[
\text{Si(OH)}_4 \cdots \text{RCHO} + \text{OH}^- \rightarrow \text{Products}
\]

In the pre-reactive structure, the OH free-radical approaches the aldehyde oxygen atom. Then, the oxygen of OH turns in the plane towards the hydrogen to be abstracted, as the energy increases to a maximum at the transition state. A product-complex is then obtained, which, in the next step, yields the final products, i.e., a water molecule and the corresponding free-radical.

Pre-reactive complex structures in the gas phase reactions have been published elsewhere for formaldehyde and acetaldehyde (Alvarez-Idaboy et al., 2001). In these complexes, the main stabilizing interactions involve (i) the OH-radical hydrogen atom with the carbonyl oxygen and (ii) the OH-radical oxygen atom with the aldehydic H atom. In the case of acetaldehyde, another possible pre-reactive complex structure was reported in which the OH-radical oxygen atom is oriented towards the –CH₃ group, but it was shown that the corresponding channel is not relevant to atmospheric chemistry in the gas phase (Alvarez-Idaboy et al., 2001). However, it could become essential when the aldehydic group is attached to a surface model. For larger aldehydes, it is possible that chain H-abstraction could become significant also in the gas phase. However, experimental gas phase rate constants are all very similar, suggesting that the main mechanism is the aldehydic abstraction in all cases. A detailed study of these gas phase reactions is in progress.

In the presence of a surface model, pre-reactive complexes will be different depending on the original adsorption complex. Starting from the ADS1 adsorption complex, the reaction mechanism will be an abstraction of the chain H atom because the aldehyde-H atom is bound to the surface, whereas from ADS2, the reaction will be the abstraction of the aldehydic H atom that is not bound to the surface.

The molecular structures of the optimized pre-reactive complexes are shown in Fig. 3 along with the most relevant non-bonding distances. In both cases, the structure of the adsorption complex remains almost unchanged. In the chain H-abstraction mechanism, named here as RC-α or RC-β according to the carbon atom type from where the

![Fig. 3. Optimized structures of the pre-reactive complexes. The non-bonding interatomic distances are in Å.](image-url)
H atom is being abstracted, the aldehyde-hydrogen atom is not available for reaction. Thus, the oxygen atom of the OH radical approaches one of the chain hydrogen atoms. In the aldehydic H-abstraction, named here RC_{ald}, the OH radical approaches the aldehydic H.

In all pre-reactive complexes, a hydrogen bond exists between the H atom of the attacking OH radical and the O atom of the aldehydes. The RC-α and RC-β pre-reactive complexes have similar shapes presenting an interaction between the OH free-radical oxygen atom and a chain hydrogen atom at about 2.4–2.6 Å. In acetaldehyde, this interaction involves a α-H atom. In all others, it is a β-H atom. On the contrary, in the RC_{ald} pre-reactive complexes, the radical interacts with an aldehydic H at an almost constant distance of 2.8 Å that is shorter than in the corresponding gas phase structures.

In all cases, the approach of the OH radical produces an increase of the O_{ald}/C1/C1/C1 H_{surf} distance with respect to the previous adsorption complexes, which is more noticeable in RC-α and RC-β than in RC_{ald}. On the contrary, this RC formation produces a shortening of the H_{alkyl}/O_{surf} distances that is more remarkable in RC-α and RC-β than in the RC_{ald} complexes.

Abstraction of hydrogen atoms from carbons δ or γ is unlikely, because the pre-reactive complexes always involve the aldehydic group, and these carbons are too far from the aldehyde center.

The transition states (TS) structures, and the main bond distances in their fully optimized geometries at M05-2X/6-311++G** level are shown in Fig. 4. In these TS the OH oxygen atom approaches the hydrogen atom to be abstracted, as the energy increases to a maximum along the reaction path. This approach causes an enlargement of the H_{OH}/O_{ald} distances, while the O_{ald}/H_{surf} distance decreases, increasing slightly the H_{alkyl}/O_{surf} distances in the TS-β complexes with respect to the previous RC structures. On the contrary, in the TS_{ald} complexes the O_{ald}/H_{surf} distance is longer than in the RC ones, while the H_{alkyl}/O_{surf} distances are similar.

Vibration modes corresponding to the imaginary frequencies at the transition states indicate that these vibrations are essentially the characteristic H atom motion between a carbon atom and the oxygen atom of the OH radical. In the TS_{ald} complexes the C···H distances (Fig. 4) are similar in all cases, and imaginary frequencies are also similar (Table 2). However, in the alkyl H-abstrac-
Table 2
Relative energies (in kcal/mol) in the OH reaction with aldehydes adsorbed on the Si(OH)₄ monomer (calculated at M05-2X/6-311++G** level).

<table>
<thead>
<tr>
<th></th>
<th>E₁</th>
<th>E₂</th>
<th>E_{TS}^{eff}</th>
<th>ΔE</th>
<th>Imag. freq.</th>
<th>α</th>
<th>β</th>
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<tbody>
<tr>
<td>Acetaldehyde + OH</td>
<td>−4.99</td>
<td>7.40</td>
<td>2.41</td>
<td>−23.11</td>
<td>−1492</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propanal + OH</td>
<td>−5.48</td>
<td>5.75</td>
<td>0.27</td>
<td>−16.42</td>
<td>−1294</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanal + OH</td>
<td>−4.89</td>
<td>3.34</td>
<td>−1.55</td>
<td>−19.67</td>
<td>−1043</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentanal + OH</td>
<td>−5.18</td>
<td>3.35</td>
<td>−1.83</td>
<td>−19.20</td>
<td>−992</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Aldehydic H-abstraction
Acetaldehyde + OH | −4.58 | 3.98 | −0.60 | −26.71 | −447 | | |
Propanal + OH | −4.64 | 3.77 | −0.86 | −26.64 | −462 | | |
Butanal + OH | −4.80 | 3.97 | −0.82 | −26.91 | −475 | | |
Pentanal + OH | −5.06 | 3.97 | −1.09 | −26.86 | −471 | | |

* Imaginary frequency of the TS in cm⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>D_{RC}</th>
<th>D_{TS}</th>
<th>D_{TSRC}</th>
<th>Imag. freq.</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde + OH</td>
<td>5.06</td>
<td>3.97</td>
<td>4.58</td>
<td>3.98</td>
<td>−26.71</td>
<td>−447</td>
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<tr>
<td>Propanal + OH</td>
<td>4.80</td>
<td>3.97</td>
<td>4.64</td>
<td>3.77</td>
<td>−26.64</td>
<td>−462</td>
</tr>
<tr>
<td>Butanal + OH</td>
<td>4.58</td>
<td>3.97</td>
<td>4.58</td>
<td>3.97</td>
<td>−26.91</td>
<td>−475</td>
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<td>5.18</td>
<td>3.34</td>
<td>−26.86</td>
<td>−471</td>
</tr>
</tbody>
</table>

* Imaginary frequency of the TS in cm⁻¹.

In acetaldehyde the H-abstraction is with the α-H atom.

The reaction energy of the alkyl H-abstraction, ΔE, is negative and very variable, and it depends on the stability of the formed radical. The optimized structures of these radicals are shown in Fig. 5. The acetyl radical presents a much larger stability than the others, because α abstraction allows for a delocalization of the unpaired electron over the double bond.

In the aldehydic H-abstraction, results are quite systematic. E_{TS}^{eff} decreases with the increase of size of the aliphatic chain, while the RC stabilization energy increases slightly. All reaction energies, ΔE, are similar and negative indicating that these reactions are energetically favored and irreversible. These ΔE values are larger than in the alkyl H-abstraction.

3.3. Reaction kinetics

The rate constants for all reactions have been determined using the Transition State Theory. In all cases the
Table 3
Calculated rate constants (in cm$^3$ molecule$^{-1}$ s$^{-1}$) and tunneling corrections ($\kappa$) at 298 K, for the H-abstraction reactions on the Si(OH)$_4$ model ($k_{\text{eff}} = \sigma K_0 k_2$).

<table>
<thead>
<tr>
<th>Alkyl H-abstraction</th>
<th>$\sigma$</th>
<th>$K_0$ ($\times 10^{-21}$)</th>
<th>$\kappa$ ($\times 10^0$)</th>
<th>$k_{\text{eff}}$ ($\times 10^{-11}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>3</td>
<td>1.12</td>
<td>12.1 0.02</td>
<td>0.0068</td>
</tr>
<tr>
<td>Propanal</td>
<td>3</td>
<td>2.89</td>
<td>6.01 0.36</td>
<td>0.30</td>
</tr>
<tr>
<td>Butanal</td>
<td>1</td>
<td>0.67</td>
<td>3.0 20.40</td>
<td>1.37</td>
</tr>
<tr>
<td>Pentanal</td>
<td>1</td>
<td>0.28</td>
<td>2.8 12.91</td>
<td>0.38</td>
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<thead>
<tr>
<th>Aldehydic H-abstraction</th>
<th>$\sigma$</th>
<th>$K_0$ ($\times 10^{-21}$)</th>
<th>$\kappa$ ($\times 10^0$)</th>
<th>$k_{\text{eff}}$ ($\times 10^{-11}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>1</td>
<td>0.24</td>
<td>1.4 9.06</td>
<td>0.22</td>
</tr>
<tr>
<td>Propanal</td>
<td>1</td>
<td>0.37</td>
<td>1.4 10.78</td>
<td>0.40</td>
</tr>
<tr>
<td>Butanal</td>
<td>1</td>
<td>0.95</td>
<td>1.4 7.63</td>
<td>0.71</td>
</tr>
<tr>
<td>Pentanal</td>
<td>1</td>
<td>1.56</td>
<td>1.4 4.41</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 4
Calculated total rate constants (in cm$^3$ molecule$^{-1}$ s$^{-1}$) and branching ratios at 298 K, for the H-abstraction reactions on the Si(OH)$_4$ model. Experimental values correspond to the gas phase reaction.

<table>
<thead>
<tr>
<th>Alkyl H-abstraction</th>
<th>$k_{\text{eff}}$ ($\times 10^{-11}$)</th>
<th>Aldehydic H-abstraction</th>
<th>$k_{\text{eff}}$ ($\times 10^{-11}$)</th>
<th>Ratio alkyl-H/ald-H</th>
<th>$k_{\text{overall}}$ ($\times 10^{-11}$)</th>
<th>$k_{\text{experimental}}$ ($\times 10^{-11}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>0.0068</td>
<td>0.22</td>
<td>3/97</td>
<td>0.23</td>
<td>1.50 $^a$, 1.44 $^b$</td>
<td></td>
</tr>
<tr>
<td>Propanal</td>
<td>0.30</td>
<td>0.40</td>
<td>43/57</td>
<td>0.70</td>
<td>1.90 $^b$, 2.06 $^c$, 1.99 $^d$</td>
<td></td>
</tr>
<tr>
<td>Butanal</td>
<td>1.37</td>
<td>0.71</td>
<td>66/34</td>
<td>2.08</td>
<td>2.88 $^c$, 2.38 $^h$, 2.38 $^d$</td>
<td></td>
</tr>
<tr>
<td>Pentanal</td>
<td>0.38</td>
<td>0.70</td>
<td>35/65</td>
<td>1.08</td>
<td>2.48 $^c$, 2.61 $^h$, 2.76 $^c$</td>
<td></td>
</tr>
</tbody>
</table>

$a$ Sivakumaram and Crowley (2003), Zhu et al. (2008).
$b$ D’Anna et al. (2001).
$c$ Thevenet et al. (2000).
$e$ Albaladejo et al. (2002).
4. CONCLUSIONS

In this work we have studied the adsorption of C2–C5 aldehydes on models of silicate surfaces and their subsequent reaction with OH radicals. For adsorption, two models were used: the Si(OH)₄ monomer, and a cyclic hexamer. Although these differ widely in size, the same two types of adsorption complexes are formed: in the ADS1 complexes, the aldehyde H interacts with a neighbouring oxygen atom, while the aliphatic chain extends away from the surface. In the ADS2 complexes, the chain hydrogen atoms interact with the surface, and the number of interactions increases with the chain length. This implies that, especially for aldehydes with more than four carbon atoms, it is interesting to use the hexamer cluster model for the adsorption studies in order to account for these interactions and to obtain good adsorption energies.

Once aldehydes are adsorbed, they may react with OH free-radicals. The use of the hexamer model to study this reaction is attractive, but it is prohibitive at this level of theory. However, in order to obtain reliable kinetic data, a high level of theory is necessary to calculate energies and partition functions. Faced with this dilemma, a pragmatic compromise must be achieved. The hexamer model describes better the adsorption but has no significant effect on the interaction of the OH radical with aldehyde, the formation of the RC and the transition states. Hence in this work, only the monomer model has been used to estimate the effect of the presence of silicates on the OH reaction with the C2–C5 aldehydes.

We observe that the OH reaction takes place according to two different mechanisms, depending on the shape of the adsorption complex. As for most radical-molecule reactions, both are complex mechanisms that involve the barrier-less initial formation of a pre-reactive complex that is in equilibrium with the adsorbed aldehyde and the OH radical. In the second step, the pre-reactive complex proceeds through the transition state to form a radical and a water molecule irreversibly.

On the basis of the calculated rate constants we conclude that the reaction of the OH free-radical with acetaldehyde, propanal, butanal and pentanal adsorbed on silicates, at atmospheric pressure, is definitely slower than the corresponding reaction in the gas phase. In the presence of a silica monomer model surface, the reaction of acetaldehyde with OH occurs mainly according to the aldehydic H-adsorption mechanism and its rate constant is about one sixth its value in the gas phase, suggesting that mineral aerosols represent a powerful sink for this compound. Starting from propanal, the chain alkyl H-abstraction becomes a competitive pathway that contributes significantly to the total rate constant, and new reaction products are expected to be obtained.

Thus, the presence of mineral particles in polluted atmospheres may play a non-negligible role in the aldehydes loss process at atmospheric pressure. Not only do they trap these molecules, and OH radicals, but they also seem to slow down the aldehydes + OH reaction and to increase the ratio between alkyl H- and aldehyde H-abstraction rates, thus yielding by-products that are different than those in the gas phase. The heterogeneous loss of aldehydes indicates that their interaction with mineral particles in the troposphere may have significant implications for the balance of these organic compounds, as well as of those compounds whose existence depends on them. Experimental results for the aldehydes + OH reactions in the presence of mineral aerosols would be useful.

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REFERENCES


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