Theoretical investigation on the role of mineral dust aerosol in atmospheric reaction: A case of the heterogeneous reaction of formaldehyde with NO2 onto SiO2 dust surface

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HIGHLIGHTS

- The heterogeneous reaction mechanism and kinetics of VOCs is revealed by DFT.
- SiO2 is a good sink for HCHO and NO2, in particular for HCHO.
- The presence of SiO2 accelerates the atmospheric reaction of HCHO with NO2.
- The loss of HCHO on dusts is significant in dusty urban and desert environments.

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ABSTRACT

The role of mineral dusts on the heterogeneous reaction of formaldehyde with NO2 was investigated using a quantum chemical approach. SiO2 was selected as a model of mineral dust to investigate the heterogeneous reaction mechanism and kinetics because the mineral dust is comprised of ~60% of SiO2. Compared with NO2, formaldehyde was easily adsorbed onto SiO2 model, indicating SiO2 was a sink for formaldehyde. Further data showed that the presence of SiO2 reduced the reaction barrier, but did not change reaction mechanism. The kinetics calculation using the canonical variational transition state theory plus small curvature tunneling correction showed that the presence of SiO2 could accelerate the atmospheric reaction rate of formaldehyde with NO2 to produce HONO. The effect of the altitudes was also considered, and the heterogeneous reaction rate decreased with increasing the altitude due to the atmospheric temperature decrease, suggesting that the degradation of atmospheric HCHO onto available mineral dusts might be competitive with the corresponding homogeneous reaction, especially in dusty urban and desert environments. This work can lay the foundation on the atmospheric heterogeneous reaction of VOCs, probe the role of mineral dust and establish the atmospheric transformation models, to better understand pollution mechanism.

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1. Introduction

An annual emission flux of mineral dusts was 1000–3000 Tg globally, which comprises nearly one-third to one-half of total...
annual aerosol emissions by the mass (Bian and Zender, 2003). The
dusts can enter various atmospheric environments through the
complicated long-range migration. Therefore, extensive attentions
have been paid to the mineral dusts due to their potential effect on
the atmospheric heterogeneous chemistry and the climate change
(Prospero, 1999). Dentener et al. (1996) reported that the
interactions of \( \text{N}_2\text{O}_5\), \( \text{O}_3\) and \( \text{HO}_2\) radicals with dust significantly
affected the photochemical oxidant cycle, causing ozone decrease up
to 10% in and near the dust source areas. McNaughton et al.
(2009) noted that nitric acid concentrations were reduced to
almost 50% in the presence of dust. All these results indicated that
mineral dusts could change the chemical balance of the atmos-
pheric pollutants by providing a reactive substrate or surface onto
or in them (Bian and Zender, 2003; Dentener et al., 1996; Galy-
Lacaux et al., 2001; Usher et al., 2003; Zhao et al., 2011).

Volatile organic compounds (VOCs) are one group of important
atmospheric pollutants, emitted from anthropogenic and biogenic
sources (Atkinson, 2000; Bourdin et al., 2014). Due to the potential
adverse effects on human health and the active involvement in the
atmospheric reactions (Ji et al., 2012), the atmospheric reactions of
VOCs have attracted significant scientific and regulatory attention.
Therefore, the homogeneous atmospheric reactions of VOCs with
various reactive species (RSSs) have been investigated in detail
currently, and significant advances were made to understand both
the kinetics and mechanisms of these reactions, as well as their
global impact on the atmosphere (Alvarez-Ildaboy et al., 2001;
Atkinson, 2000; Atkinson and Arey, 2003; Stemmler et al., 1997).

Recently, a few laboratory studies attempted to investigate the
heterogeneous reactions of simple VOCs onto the mineral dusts,
and the strong interactions can be found between the mineral
particulates and VOCs in addition the significant influence of mineral
dusts onto the atmosphere (McNaughton et al., 2009; Zhao et al.,
2011, 2010). However, little is known about the heterogeneous re-
action of various RSSs with adsorbed VOCs onto the atmospheric
dusts as well as the impact of the mineral dusts on the heteroge-
neous reaction both from experimental and theoretical aspects.

This study focuses on the examination of the heterogeneous re-
action of formaldehyde (HCHO) with nitrogen dioxide (\( \text{NO}_2\)) onto
silica (\( \text{SiO}_2\)) particles, the major oxide constituent of mineral dusts
(≥60%). HCHO is one of the most prevalent VOCs in the Earth's
atmosphere. It can be produced by the photooxidation of most
VOCs and serve as an important source of \( \text{HO}_2\) radical (Lin et al.,
2012), peroxy radicals, and peroxyacyl nitrates (Carlos-Cuellar
et al., 2003). Therefore, its dual role makes it as an important
constituent of the natural unpolluted atmosphere, but also one of
the major pollutants from anthropogenic sources such as motor
vehicles (Power et al., 2011), power plants (Jurkat et al., 2011) and
combustion process (Zhang et al., 2006). Thus, it has taken a great
deal of research to the reaction of HCHO and \( \text{NO}_2\) in the absence of
\( \text{SiO}_2\) (Ji et al., 2012; Xu and Lin, 2003) or to the adsorption per-
formance of HCHO onto \( \text{SiO}_2\) (Carlos-Cuellar et al., 2003; Iuga et al.,
2008), but to our knowledge, no prior theoretical and experi-
mental studies have been explored the heterogeneous reaction of
HCHO with \( \text{NO}_2\) in the presence of \( \text{SiO}_2\). The goals of this study are
as follows: (i) find a reasonable theoretical method to model the
heterogeneous reaction of VOCs; (ii) specify which species is more
easily absorbed onto the mineral dust aerosol surface: organic or
inorganic compounds; (iii) probe the role of mineral dust aerosol on
the atmospheric reaction.

2. Methods

All quantum chemical calculations were performed with the
Gaussian 03 programs package (Frisch et al., 2003). As a part of our
ongoing study, the MPWB1K method (Zhao and Truhlar, 2004) was
also used in this work, which has been already employed to suc-
cessfully calculate the homogenous reactions of VOCs with RSSs (Ji
et al., 2012). The geometrical parameters of all stationary points
were calculated with a standard 6-311G(d,p) basis set, and here-
inafter the employed function level was denoted as MPWB1K/6-
311G(d,p) level. All stationary points were allowed to move freely
until reaching the optimal site. Combined with the vibrational
analysis, the nature of each point on the potential energy surface
(PES) was characterized to confirm the calculated geometry cor-
responding to a saddle point with only one imaginary frequency or
a local minimum without imaginary frequency. Intrinsic reaction
coordinate (IRC) calculations (Gao et al., 2014) were performed to
confirm that the transition state structures connected the reactants
with products. The PES was further refined by MPWB1K/6-311+G(3df, 3pd) level to yield more accurate energetic
information.

To further test the accuracy of MPWB1K method, Ab Initio and
other density functional theory (DFT) methods, including MP2,
CASSCF(T), and B3LYP methods, were employed for the single point
calculation. For simplicity, the dual-level approach was denoted as
\( \text{X}/\text{Y} \), where a single-point energy calculation at level \( \text{X} \) is carried
out for the geometry optimized at a lower level \( \text{Y} \). For energy cal-
culations, the basis set superposition error (BSSE) and zero point
energy (ZPE) corrections were considered and discussed, respec-
tively, and the full discussion is provided in Supporting Information
(Table S1). The comparison shows that the MPWB1K//MPWB1K
level of theory got a balance between the accuracy and the
computational cost.

The concentration could be estimated using the theoretical
formula as follows:

\[
[\text{Adsorption complex}] = K_c \left[ \text{Species 1} \right] \left[ \text{Species 2} \right]
\]

where [Adsorption complex] and [Species] are average concentra-
tion of corresponding species; \( K_c \) is the calculated equilibrium
constant (Iuga et al., 2010a). Herein, \( K_c = \text{exp}(-\Delta G/RT) \), where \( R \) is
the gas constant, \( T \) is the temperature, and \( \Delta G \) is the binding Gibbs
free energy calculated as:

\[
\Delta G = G_{\text{Adsorption complex}} - \left( G_{\text{Species 1}} + G_{\text{Species 2}} \right)
\]

For kinetics calculations, the dual-level potential profile along
with the reaction pathway is further refined with the interpolated
single-point energy (ISPE) method (Chuang et al., 1999), where a
few extra single-point calculations are needed to correct the lower-
level reaction path. Using the Polyrate program (Corchado et al.,
2002), the rate constants and product distributions of all the
possible reaction pathways were calculated using canonical vari-
ational transition state theory (CVT) (Truhlar and Garrett, 1980) with
a small curvature tunneling correction (Liu et al., 1993). The rate
constant can be obtained by variationally minimizing the general-
ized transition-state theory rate constant \( k^{\text{CVT}}(T) \) with respect to
the dividing surface at \( s \). That is,

\[
k^{\text{CVT}}(T) = \min_T k^{\text{GT}}(T, s)
\]

\[
k^{\text{GT}}(T, s) = \sigma \frac{Q^{\text{GT}}(T, s)}{Q^k(T)} \exp \left( -\beta V_{\text{MEP}}(s) \right)
\]

In Eqs. (1) and (2), \( s \) is the location of the generalized transition
state on IRC; \( \sigma \) is the symmetry factor accounting for the possibility
of two or more symmetry-related reaction paths; \( \beta \) equals \((k_B T)^{-1}\)
where \( k_B \) is Boltzmann’s constant, \( h \) is Planck’s constant; \( Q^e(T) \) is the
reactant’s partition function per unit volume, excluding symmetry
numbers for rotation; \( V_{\text{MEP}}(s) \) is the classical energy along with the
minimum-energy path (MEP) overall zero of energy at the re-
antacts; \( Q^e(T)s \) is the partition function of generalized transition
state at \( s \) with the local zero of energy at \( V_{\text{MEP}}(s) \) and with all
rotational symmetry numbers set to unity. To include the tunneling
effect, the CVT rate constant is multiplied by a transmission coef-
ficient computed with the small-curvature tunneling (SCT)
approximation, which is denoted by \( k^{\text{CVT}}(s) \). For the SCT calcula-
tions, the effective reduced mass is obtained by a sixth-order
Lagrangian interpolation. The Euler single-step integrator with a
step size of 0.0005 \((\text{amu})^{1/2} \text{ bohr}\) is used to follow the MEP. The
generalized normal-mode analysis is performed for each 0.05
\((\text{amu})^{1/2} \text{ bohr}\).

3. Results and discussion

3.1. Adsorption mechanisms

3.1.1. Surface model

On the earth, the majority of composition of clay fraction is
phyllloclaylates, and the coarser particles mainly consist of quartz.
This results in a large abundance of SiO\(_2\) in the atmosphere. In the
nature, the surface of most SiO\(_2\) powders and gels is made of silanol
hydroxyg groups (SiOH), formed by extremely small particles of
silica or by porous aggregates (Pereira et al., 1999a). Thus, the
natural clay mineral, such as phyllosilicate, is abundant with a large
number of siloxane Si–O–Si bridges and SiOH on the surface. As
such, silicic acid is regarded as the best model for SiO\(_2\) mineral
dusts (Civalleri et al., 1998; Iuga et al., 2010b, 2008; Pereira et al.,
1999b).

To more closely clarify the real model of silicic acid, three silica-
based clusters of the Si\(_3\)O\(_6\)(OH)\(_2\), Si(OH)\(_4\), Si\(_3\)O\(_2\)(OH)\(_8\),
and Si\(_6\)O\(_8\)(OH)\(_{12}\), were established in this work, which are respectively
stood for the monomeric, linear, and cyclic patterns of silicic acid.
The corresponding structures of three patterns were modeled at
MPW1B1K/6-311G(d,p) level (Fig. 1), as well as the results calculated
by B3LYP/6-311G(d,p) and MP2/6-311G(d,p) levels. The optimized
parameters obtained by the above three levels were reasonably
consistent with each other, and the largest discrepancies were
0.01 Å in the bond lengths and 0.1° in the bond angles.

For the monomeric Si(OH)\(_4\) (Fig. 1), all Si–O and H–O bonds
were 1.63 and 0.95 Å, respectively, and all O–Si–O angles were
106.3°. Thus, it belongs to S\(_4\) point group. For the linear trimer,
Si\(_3\)O\(_2\)(OH)\(_8\), C\(_1\) conformation was obtained, meaning that Si, H and
O atoms were not equivalent. Thus, the Si–O bonds and the
O–Si–O angles varied from 1.61 to 1.63 Å and from 103.9° to 146.3°,
and the H–O bonds were maintained at approximately 0.95 Å. For
the cyclic hexamer, Si\(_6\)O\(_8\)(OH)\(_{12}\), a “crown” with highly symmetry
(S\(_6\) point group) was observed, and the Si–O bonds in the bridge
were always 1.64 Å, but those in terminal group were 1.61–1.64 Å.
The last result was in good agreement with the experimental data
of 1.64 Å for pyrophyllite (Lee and Guggenheim, 1981) and 1.62 Å for
muscovite minerals (Guggenheim et al., 1987).

Among of three models, it is found that the surfaces are abund-
ient with a large number of siloxane Si–O–Si bridges and SiOH
group, especially in the Si\(_3\)O\(_2\)(OH)\(_8\) model, which could form
hydrogen bond interaction (H-bond) between HCHO and NO\(_2\). Throughout this work, the atoms in three models were denoted as a
subscript Si, and the atoms in HCHO/NO\(_2\) molecule were marked as a
subscript HCHO/NO\(_2\).

To better probe the adsorption property of three surface models,
the natural bond orbital (NBO) charge distributions were calculated
(Fig. 2). In three surface models, the more positive of the charge
distribution of H atom is, the more prone to forming H-bond with O
atom (HCHO or NO\(_2\)). And the more negative of the charge dis-
tribution of O atom is, the more preferred to form H-bond with H
atom is. For the monomer Si(OH)\(_4\), the NBO of each OSi and HSi atom
were –0.616 and 0.303 e, respectively, suggesting that each OSi or
HSi atoms in the monomer have equal opportunity to form H-bonds
with the reactants. For the linear trimer, Si\(_3\)O\(_2\)(OH)\(_8\), the NBO of
siloxane OSi(2) and OSi(5) atoms were all –0.777 e, which were
more negative than other O atoms by 0.109 e. However, the pres-
bence of two O atoms within Si\(_3\)O\(_2\)(OH)\(_8\) made it diffi-
cult to form a hydrogen bond interaction (H-bond) between HCHO
and NO\(_2\). Throughout this work, the atoms in three models were denoted as a
subscript Si, and the atoms in HCHO/NO\(_2\) molecule were marked as a
subscript HCHO/NO\(_2\).

As Fig. 2 shows, the cyclic hexamer, Si\(_6\)O\(_8\)(OH)\(_{12}\) looks like a
“blooming flower”. The NBO of OSi and HSi atoms on the petal were
all –0.683 and 0.330 e. These data were more negative or more
positive than other OSi or HSi atoms, thereby preferring to form H-
bond with H or O atoms of the reactants. As discussed above, the

Fig. 1. The optimized cluster models at the MPW1B1K/6-311G(d,p), B3LYP/6-311G(d,p) and MP2/6-311G(d,p) levels. (Bond lengths are in angstroms and angles are in degrees.)
3.1.2. Adsorption model of reactants onto mineral surface

Under atmospheric conditions, HCHO and NO$_2$ have the opportunities to be adsorbed onto the SiO$_2$ surface. Therefore, it is necessary to estimate the adsorption amount and adsorption model of HCHO as well as NO$_2$ onto SiO$_2$, and to specify which atmospheric pollutant, HCHO or NO$_2$, is more easily adsorbed onto the surface. Herein, the monomer Si$_4$(OH)$_4$ was used as an example to answer these questions. For HCHO, two adsorption types could be found. For the first one, the O$_{HCHO}$ atom is attracted to a H$_3$, thus H$_{HCHO}$ atom interacts with O$_5$ on the surface (ADS-1-HCHO). For the second one, HCHO interacts with the surface through both of its H$_{HCHO}$ atoms (ADS2-HCHO). The corresponding geometries are presented in Fig. 3. The O$_{HCHO}$—H$_3$ bond was only obtained in ADS-1-HCHO with 1.89 Å, and the H$_{HCHO}$—O$_5$ distances were 2.51–2.95 Å in ADS-1-HCHO and 2.71–2.89 Å in ADS2-HCHO, respectively. The adsorption distances in ADS2-HCHO were larger than those in ADS-1-HCHO, suggesting that weaker interactions could be obtained in ADS2-HCHO. Combined with the adsorption energy ($\Delta E_{ad}$) (Fig. 3), the $\Delta E_{ad}$ of ADS-1-HCHO was $-5.32$ kcal mol$^{-1}$, which was by 3.91 kcal mol$^{-1}$ larger than that of ADS2-HCHO. These results indicate that in the atmosphere, HCHO would likely be adsorbed onto SiO$_2$ as the ADS-1-HCHO adsorption type. That is, the O$_{HCHO}$ atom of C=O group, with highly polar, is perpendicularly trap in a silanol hydrogen atom to form ADS-1-HCHO.

In case of NO$_2$, only one possible adsorption type can be obtained (ADS-NO$_2$), with both O$_{NO2}$ atoms interacting with H$_3$ atoms (Fig. 3). Two O$_{NO2}$—H$_3$ distances of 3.22 and 2.18 Å were larger by 0.29 and 1.33 Å than those of ADS-1-HCHO, suggesting weaker interactions in ADS-NO$_2$. Adsorption energy showed the similar results (Fig. 3). For example, the $\Delta E_{ad}$ of ADS-1-HCHO was approximately 3 kcal mol$^{-1}$ more negative than that of ADS-NO$_2$ ($-2.48$ kcal mol$^{-1}$). In general, the adsorption interaction and the energy of ADS-1-HCHO were stronger than those of ADS-NO$_2$, indicating that HCHO was more easily adsorbed onto the surface model.

Furthermore, a comparison between the amount of ADS-1-HCHO and ADS-NO$_2$ is presented in Table S2. According to the Formula (1), the following equations could be obtained:

$$[\text{ADS-1-HCHO}] = K_{C1}[\text{HCHO}]$$

$$[\text{ADS-NO}_2] = K_{C2}[\text{NO}_2]$$

Due to the [ADS] cannot be quantified in the atmosphere, the ratios of [ADS-1-HCHO] and [ADS-NO$_2$] can be written as

$$[\text{ADS - HCHO}] = K_{C1}[\text{HCHO}]$$

$$[\text{ADS - NO}_2] = K_{C2}[\text{NO}_2]$$

Where, [HCHO] and [NO$_2$] were assumed to be $5.15 \times 10^{14}$ molecule cm$^{-3}$ (13.7 $\mu$g m$^{-3}$) and $1.02 \times 10^{15}$ molecule cm$^{-3}$ (42.2 $\mu$g m$^{-3}$), respectively, which is the annual average gaseous concentrations in China measured by Lu et al. (2010) and Yang et al. (2010). Therefore, the ratios of [ADS-1-HCHO] and [ADS-NO$_2$] were derived from Eq. (6), and the results as well as $K_{C1}$ and $K_{C2}$ are presented in Table S2. The ratios of [ADS1-HCHO] and [ADS-NO$_2$] varied from 1.83 $\times$ $10^{-3}$ to 4.72 $\times$ $10^{-4}$ within the temperature range of 217–298 K. This means that the concentrations of ADS1-HCHO were by 3–4 orders of magnitude larger than those of ADS-NO$_2$, and thus, ADS-1-HCHO is a more important conformation than ADS-NO$_2$ under atmospheric conditions. This result matches well with known adsorption structures and energy, further confirming that SiO$_2$ traps HCHO more easily than NO$_2$.

As discussed above, ADS-HCHO is more important than ADS-NO$_2$.
in the atmosphere. Therefore, we focused on the study of HCHO adsorptions onto three surface models (Si(OH)₄, Si₃O₂(OH)₈, and Si₆O₆(OH)₁₂), and the formed adsorption complexes were denoted as 1-ADS, 3-ADS and 6-ADS, respectively. The corresponding geometries and E_aes are listed in Fig. 4 and Table S3. For HCHO adsorption onto three surface models, one OHCHO e HSi bond and two HHCHO e OSi bonds were observed (Fig. 4), indicating that the surface model size did not significantly affect the adsorbed structures of HCHO. For example, the OHCHO e HSi bond of 1-ADS was 1.89 Å and elongated only 0.09 Å in 6-ADS. From Table S3, the E_aes of 1-ADS, 3-ADS, and 6-ADS were observed to be −5.32, −6.76, and −5.92 kcal mol⁻¹, respectively. Although there are some differences among them, the outside H atom which is free to be attacked by NO₂ is similar for three surface models. Therefore, it can be hopefully assumed that the slight increase in the adsorption energy did not affect significantly the energy barriers of the heterogeneous reaction. Increasing the model size of SiO₂ requires significantly the computational time. As for 6-ADS, the conducting geometry and energy calculations at the MPWB1K method, the CPU time required approximately 49 and 27 h on our workstation, respectively, while the corresponding computing times were only about 33 and 35 min for 1-ADS. As such, in this study, the monomer Si(OH)₄ was employed as the surface model to investigate the following heterogeneous reaction. The exothermic adsorption energies indicated that all three surface models effectively captured HCHO. That is, the mineral dusts represented a powerful sink for atmospheric HCHO. Therefore, the heterogeneous reaction between NO₂ and adsorbed HCHO onto SiO₂ particles was expected to have potentially significant impacts on the Earth’s atmosphere.

3.2. Reaction mechanism and kinetics of HCHO and NO₂ on surface model

According to the above results, HCHO was found to be more easily trapped by SiO₂ surface, thus in the following study, the heterogeneous reaction of NO₂ with the adsorbed HCHO was considered although adsorbed NO₂ may be also reacted with other atmospheric pollutants (Goodman et al., 1999; Ma et al., 2011). According to the above HCHO-surface adsorbate (1-ADS), two different channels were considered. The first channel is H-abstraction, with both syn-H-abstraction and anti-H-abstraction by ONO₂ atom (Abs_syn-O and Abs_anti-O channels) and H-abstraction by NNO₂ atom (Abs_N). The other channel is NO₂-addition with the CHCHO atom attacked by NO₂. However, for the NO₂-addition channel, the minimum energy pathway failed to locate any new transition state structures with MPWB1K, B3LYP, and MP2 methods in this work. Combined with the structures in Fig. 4, once HCHO was adsorbed on the surface, NO₂ had difficulty to approach the C atom of HCHO due to the steric effect. Meanwhile, our previous theoretical investigation about the homogeneous reaction of HCHO and NO₂ indicates that the NO₂-addition channel had much higher activation energy than H-abstraction channel. As such, its rate constant was about 10 orders of magnitude smaller than that of H-abstraction channel under the atmospheric conditions (Ji et al., 2012). Given this, only abstraction pathways were considered in the present work.

Fig. 5 and Fig. S1 display the geometries of stationary points involved in H-abstraction channels by means of fully optimized geometries at MPWB1K/6-311G(d,p) level. To understand the property of transition states (TSs), the geometry parameters (L) of the corresponding TSs were calculated using the formula

\[ L = \overline{d} (C\text{-}H)/\overline{d} (H\text{-}O\text{/N}) \]  

(Ji et al., 2013), where \( \overline{d} (C\text{-}H) \) is the variation...
in the breaking bond distance between TSs and the reactants, and $\delta$(H–X) is the forming bond distance between TSs and the products (Table S4). $\Delta$Es were 0.67, 0.27, and 1.41 for $TS_{syn-O}$, $TS_{anti-O}$, and $TS_N$, respectively. For comparison, the corresponding $\Delta$Es (Ji et al., 2012) in the homogeneous reaction are also listed in Table S4. Except for $TS_N$, the structures of $TS_{syn-O}$ and $TS_{anti-O}$ were different from those in the homogeneous reaction. For example, $\Delta$Es were 0.55, 0.30 and 1.41 for $TS_{syn-O}$, $TS_{anti-O}$, and $TS_N$, respectively, in gas-phase reaction. This indicates that the structures of $TS_{syn-O}$ and $TS_{anti-O}$ were different in the absence and presence of SiO$_2$. Therefore, their potential barriers likely underwent some changes in the presence of SiO$_2$.

The potential barriers ($\Delta$Es) and the reaction energies of three H-abstraction channels are all summarized in Table S5. The $\Delta$E of $Abs_{anti-O}$ channel was 27.94 kcal mol$^{-1}$, which was at least 6 kcal mol$^{-1}$ higher than $Abs_{syn-O}$ and $Abs_N$ channels. This indicates that the former channel may have difficulty to occur in the atmosphere. As for $Abs_{syn-O}$ and $Abs_N$ channels, the $\Delta$Es were 19.61 and 21.88 kcal mol$^{-1}$, respectively. The $\Delta$E of the former channel was lower by 2.27 kcal mol$^{-1}$ than that of the latter channel, suggesting that once HCHO is adsorbed on the surface, $Abs_{syn-O}$ channel will preferentially occur to form nitrous acid (HONO) and formyl radical that remain attached to the dust surface. However, it is well known that HONO may be mutagenic reagent (Kleffmann, 2007) and cause carcinogenic harm to humans (Kleffmann, 2007), as well as favor the acid deposition (Lu et al., 2000). Meanwhile, HONO also plays a very important role in the formation of secondary aerosols in the morning (Li et al., 2010). Therefore, the heterogeneous reaction of HCHO with NO$_2$ may be relevant to the increasing levels of atmospheric pollution.

To probe the effect of SiO$_2$ particles, the $\Delta$Es in the absence of SiO$_2$ were also calculated by our previous study (Ji et al., 2012) and also include in Table S5. The $\Delta$E of $Abs_N$ channel was only 0.54 kcal mol$^{-1}$ lower than that of the homogeneous reaction, and the $\Delta$E of other two channels were approximately 2 kcal mol$^{-1}$ smaller than those of the homogeneous reaction. This result was also consistent with those of the structures. That is, the $\Delta$E of $Abs_N$ channel did not vary largely relative to the homogeneous reaction, while the $\Delta$Es of other two channels ($Abs_{syn-O}$ and $Abs_{anti-O}$ channels) would be different between the homogeneous and heterogeneous reaction. As Table S5 shows, the $\Delta$Es of three H-abstraction channels all declined when SiO$_2$ was present, but the order of $\Delta$Es was as same as those in the homogeneous reaction: $\Delta$E($Abs_{syn-O}$) < $\Delta$E($Abs_N$) < $\Delta$E($Abs_{anti-O}$). The mechanism is clearly the same as the homogeneous reaction, suggesting that SiO$_2$ just reduced the reaction barrier but did not change the reaction mechanism.

As discussed above, compared with the homogeneous reaction, the $\Delta$Es of all three channels was slightly lower, which may lead to an enhancement of rate constants in the presence of SiO$_2$ particles. Therefore, the rate constants of $Abs_{syn-O}$, $Abs_{anti-O}$, and $Abs_N$ channels as well as the total rate constants were calculated within the temperature range of 217–298 K to simulate the temperatures in all parts of the troposphere (Table 1). For simplicity, hereinafter they were denoted as $k_{syn-O}$, $k_{anti-O}$, $k_N$, $k_{total}$, respectively. The total rate constants were obtained by summing the partial rate constants of three channels. That is, $k_{total}$ = $k_{syn-O}$ + $k_{anti-O}$ + $k_N$. Fig. S2 displays the temperature dependence of the branching ratios ($\Gamma$) of three channels. As Table 1 shows, the rate constants of three specific channels, as well as the $k_{total}$, all increased as the temperature rises. For example, the $k_{total}$ increased from 4.22 $\times$ $10^{-28}$ to 5.26 $\times$ $10^{-25}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ as the temperature increased from 217 to 298 K, indicating that increasing temperature promoted the heterogeneous reaction rate. Because there are no data about the titled heterogeneous reaction, the modified Arrhenius formula was simulated as $k = 8.45 \times 10^{-17}$ exp($-5647.50/T$) cm$^3$ molecule$^{-1}$ s$^{-1}$ within the atmospheric temperature range of 217–298 K. From this formula, the rate constants at a specified temperature point and the activation energy could be easily obtained. These theoretical calculations will facilitate the understanding the impact of this reaction on the atmosphere, when there is without experimental results.

As Table 1 shows, the rate constant of $Abs_{syn-O}$ Channel was calculated to be 5.21 $\times$ $10^{-25}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, which was 2–6 orders of magnitude faster than $Abs_{anti-O}$ and $Abs_N$ channels. Fig. S2 shows that the $\Gamma$ of $Abs_{syn-O}$ channel almost equaled to 1 in the measured temperature range of 217–298 K. This means that $Abs_{syn-O}$ channel was the predominant or exclusive pathway, and other two channels are difficult in happening in the atmosphere. Therefore, nitrous acid (HONO) and formyl radical formed from $Abs_{syn-O}$ channel are believed to be the main products within the temperature range investigated, and the latter product formyl radical will remain attached to the surface due to low evaporation.

The data of the homogeneous reaction in Table 1 show that the rate constant of the homogeneous reaction was 1.67 $\times$ $10^{-25}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, 3 times lower than that of the heterogeneous reaction. This indicates that the presence of SiO$_2$ could accelerate the atmospheric reaction rate of HCHO with NO$_2$, and enhance the yield of HONO. This could facilitate the formation of secondary aerosols and deteriorate the atmospheric
environments.

4. Atmospheric implications

The atmospheric temperature will drop approximately 6.49 K for every km when the altitude was elevated in the troposphere, and then the temperature will remain at 216.69 K in the stratosphere (from 11 km height above the earth surface) (Ji et al., 2013). Therefore, to evaluate the species rate constants at different atmospheric heights where the heterogeneous reaction of HCHO with NO2 occurred, the relationship between the rate constants and the different atmospheric heights were attempted (Fig. 6). From the figure, as the altitude increases from 0 to 12 km, the total rate constants decreased from $5.26 \times 10^{-25}$ to $4.22 \times 10^{-28}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This means that the reaction rate reduced with the increase in the atmospheric height, as compared with the ground level. Of course, the VOCs and mineral dusts concentrations will both obviously decrease as the altitude rise. As such, the influence of the title reaction on the higher atmospheric height required further experiments.

As discussed above, it can be found that the calculated rate constant for the reactions of formaldehyde with NO2 are lower than that with OH radical in the troposphere, whereas in some special regions of the developing country, for example the Pearl River Delta, South China, the formation of formaldehyde and NO2 are still very huge. Furthermore, dust storms have become a distinct feature in many regions of China. Thus, the investigation of their heterogeneous reactions on SiO2 surface may be help us to better understanding of air pollution mechanism in these polluted areas.

5. Conclusions

In this work, we have studied the adsorption mechanism of HCHO and NO2 onto SiO2 particles, as well as the heterogeneous reaction mechanism and kinetics of NO2 reacted with adsorbed HCHO. An effective method (MPWB1K) were put forward to predict the rate constants and to probe the mechanisms of the heterogeneous chemical reactions. The monomeric, linear, and cyclic silica-based clusters were established. Adsorption mechanism shows that SiO2 was an important sink for atmospheric pollutants formaldehyde and NO2, especially for formaldehyde. Although three clusters differ slightly in size and adsorption energy, the outside H atom that is free to be attacked by NO2 is the similar. Thus, the same two types of adsorption complexes are formed: ADS1–HCHO and ADS2–HCHO. That is, the slight different in size and adsorption energy did not significantly affect the subsequent heterogeneous reaction.

From reaction mechanism, three different H-abstraction channels were considered, according to the HCHO-surface adsorbate: syn-H-abstraction and anti-H-abstraction by O$_{Na}$ atom (Abs$_{syn-O}$ and Abs$_{anti-O}$ channels) as well as H-abstraction by N$_{O}$ atom (Abs$_{N}$). The order of $\Delta E$ was obtained as $\Delta E$(Abs$_{syn-O}$) < $\Delta E$(Abs$_{N}$) < $\Delta E$(Abs$_{anti-O}$), and the acyl radical and HONO are all found as the dominated intermediates.

Kinetics calculated in the temperature range of 217–298 K shows that increasing temperature promotes the heterogeneous reaction of HCHO with NO2. The rate constants of the heterogeneous reaction were 3–8 times larger than that of the homogeneous reaction within the atmospheric heights of 0–12 km, indicating that the presence of SiO2 could accelerate the atmospheric reaction of HCHO with NO2 to form a secondary aerosol precursor (HONO) in the troposphere. Furthermore, this means the elimination of atmospheric HCHO on available mineral dusts was faster than the corresponding homogeneous reactions, especially in dusty urban and desert environments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.12.044.

References


