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Heterogeneous reaction of $ClONO_2$ with TiO_2 and SiO_2 aerosol particles: implications for stratospheric particle injection for climate engineering

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Abstract. Deliberate injection of aerosol particles into the stratosphere is a potential climate engineering scheme. Particles injected into the stratosphere would scatter solar radiation back to space, thereby reducing the temperature at the Earth's surface and hence the impacts of global warming. Minerals such as TiO_2 or SiO_2 are among the potentially suitable aerosol materials for stratospheric particle injection due to their greater light-scattering ability than stratospheric sulfuric acid particles. However, the heterogeneous reactivity of mineral particles towards trace gases important for stratospheric chemistry largely remains unknown, precluding reliable assessment of their impacts on stratospheric ozone, which is of key environmental significance. In this work we have investigated for the first time the heterogeneous hydrolysis of $ClONO_2$ on TiO_2 and SiO_2 aerosol particles at room temperature and at different relative humidities (RHs), using an aerosol flow tube. The uptake coefficient, $\gamma(ClONO_2)$, on TiO_2 was $\sim 1.2 \times 10^{-3}$ at 7 % RH and remained unchanged at 33 % RH, and increased for SiO_2 from $\sim 2 \times 10^{-4}$ at 7 % RH to $\sim 5 \times 10^{-4}$ at 35 % RH, reaching a value of $\sim 6 \times 10^{-4}$ at 59 % RH. We have also examined the impacts of a hypothetical TiO_2 injection on stratospheric chemistry using the UKCA (United Kingdom Chemistry and Aerosol) chemistry–climate model, in which heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ on TiO_2 particles is considered. A TiO_2 injection scenario with a solar-radiation scattering effect very similar to the eruption of Mt Pinatubo was constructed. It is found that, compared to the eruption of Mt Pinatubo, TiO_2 injection causes less ClO_x activation and less ozone destruction in the lowermost stratosphere, while reduced depletion of N_2O_5 and NO_x in the middle stratosphere results in decreased ozone levels. Overall, no significant difference in the vertically integrated ozone abundances is found between TiO_2 injection and the eruption of Mt Pinatubo. Future work required to further assess the impacts of TiO_2 injection on stratospheric chemistry is also discussed.

1 Introduction

Climate engineering (also known as geoengineering), the deliberate and large-scale intervention in the Earth's climatic system to reduce global warming (Shepherd, 2009), has been actively discussed by research communities and is also beginning to surface in the public consciousness. The injection of aerosol particles (or their precursors) into the stratosphere to scatter solar radiation back into space is one of the solar-radiation management (SRM) schemes proposed for climate engineering (Crutzen, 2006). Sulfuric acid particles, due to their natural presence in the stratosphere (SPARC, 2006), have been the main focus of stratospheric particle injection research (Crutzen, 2006; Ferraro et al., 2011; Kravitz et al., 2013; Tilmes et al., 2015; Jones et al., 2016). Very recently, minerals with refractive indices higher than sulfuric acid, e.g. TiO_2 and SiO_2, have been proposed as possible alternative particles to be injected into the stratosphere for climate engineering (Pope et al., 2012). For example, the refractive index at 550 nm is 2.5 for TiO_2 and 1.5 for stratospheric sulfuric acid particles. If the size of TiO_2 particles used for SRM can be optimised, it is estimated that compared to sulfuric acid particles, the use of TiO_2 requires a factor of ~ 3 less in mass (and a factor of ~ 7 less in volume) in order to achieve the same solar-radiation scattering effect (Pope et al., 2012).

Injecting particles into the stratosphere would increase the amount of aerosol particles in the stratosphere, thus increasing the surface area available for heterogeneous reactions (e.g. Reactions R1a, R1b and R1c), whose effects on stratospheric chemistry and in particular on stratospheric ozone depletion have been well documented for sulfuric acid particles (Molina et al., 1996; Solomon, 1999). The background burden of sulfuric acid particles in the stratosphere, i.e. during periods with low volcanic activities, is 0.65 ± 0.2 Tg (SPARC, 2006). The eruption of Mt Pinatubo in 1991 delivered an additional ~ 30 Tg sulfuric acid particles into the stratosphere (Guo et al., 2004) and subsequently produced record low levels of stratospheric ozone (McCormick et al., 1995), in addition to causing substantial surface cooling (Dutton and Christy, 1992). Observation and modelling studies have further suggested that, after the eruption of Mt Pinatubo, significant change in the partitioning of nitrogen and chlorine species in the stratosphere occurred (Fahey et al., 1993; Wilson et al., 1993; Solomon, 1999), caused by heterogeneous reactions of N_2O_5 and $ClONO_2$ (Reactions R1a–R1c):

$$N_2O_5 + H_2O + \text{surface} \rightarrow HNO_3 + HNO_3, \tag{R1a}$$

$$ClONO_2 + H_2O + \text{surface} \rightarrow HNO_3 + HOCl, \tag{R1b}$$

$$ClONO_2 + HCl + \text{surface} \rightarrow HNO_3 + Cl_2. \tag{R1c}$$

Therefore, before any types of material can be considered for stratospheric particle injection, their impact on stratospheric chemistry and ozone in particular has to be well understood (Tilmes et al., 2008; Pope et al., 2012).

Heterogeneous reactions on sulfuric acid and polar stratospheric clouds (PSCs) have been extensively studied and well characterised (Crowley et al., 2010; Ammann et al., 2013; Burkholder et al., 2015). However, the reactivity of minerals (e.g. TiO_2 and SiO_2) towards reactive trace gases in the stratosphere has received much less attention. For example, the heterogeneous reactions of $ClONO_2$ with silica (SiO_2) and alumina (Al_2O_3) in the presence of HCl (Reaction R1c) have only been explored by one previous study (Molina et al., 1997), in which minerals coated on the inner wall of a flow tube were used. Further discussion of this work is provided in Sect. 4.4. The lack of high-quality kinetic data for important reactions impedes reliable assessment of the impact of injecting mineral particles into the stratosphere on stratospheric ozone (Pope et al., 2012). TiO_2 is an active photocatalyst (Shang et al., 2010; Chen et al., 2012; Romanias et al., 2012; Kebede et al., 2013; George et al., 2015), and the effects of its photochemical reactions on stratospheric chemistry, if injected into stratosphere for the purpose of climate engineering, have never been assessed. Therefore, its atmospheric heterogeneous photochemistry deserves further investigation.

To address these issues, in our previous work we have investigated the heterogeneous reactions of N_2O_5 with TiO_2 (Tang et al., 2014c) and SiO_2 (Tang et al., 2014a) particles (Reaction R1a). That work is extended here to the investigation of the heterogeneous hydrolysis of $ClONO_2$ on TiO_2 and SiO_2 (Reaction R1b) using an aerosol flow tube. There are only a few previous studies in which the reactions of $ClONO_2$ with airborne particles or droplets have been examined. For example, the interaction of $ClONO_2$ with sulfuric acid aerosol particles has been investigated using aerosol flow tubes (Hanson and Lovejoy, 1995; Ball et al., 1998; Hanson, 1998). Droplet train techniques have been used to study the heterogeneous reactions of $ClONO_2$ with aqueous droplets containing sulfuric acid (Robinson et al., 1997) or halide (Deiber et al., 2004). The interaction of $ClONO_2$ with airborne water ice particles has also been examined (Lee et al., 1999). Our experimental work, carried out at room temperature and at different relative humidities (RHs), is the first study which has investigated the heterogeneous interaction of $ClONO_2$ with airborne mineral particles. In the lower stratosphere into which particles would be injected, typical temperature and RH ranges are 200–220 K and $< 40\,\%$, respectively (Dee et al., 2011). We note that, while our experimental work covers the RH range relevant for the lower stratosphere, it has only been performed at room temperature instead of 200–220 K due to experimental challenges.

$ClONO_2$ may also play a role in tropospheric chemistry (Finlayson-Pitts et al., 1989), though its presence in the troposphere has not yet been confirmed by field measurements. The importance of Cl atoms in tropospheric oxidation capacity has received increasing attention in recent years (Simpson et al., 2015), and precursors of Cl atoms – e.g. $ClNO_2$ (Osthoff et al., 2008; Thornton et al., 2010; Phillips et al., 2012; Bannan et al., 2015; Wang et al., 2016), Cl_2 (Spicer et al., 1998; Riedel et al., 2012; Liao et al., 2014) and HOCl (Lawler et al., 2011) – have been detected in the troposphere at various locations. Cl atoms react with O_3 to form ClO radicals, which react with NO_2 to produce $ClONO_2$. The uptake of $ClONO_2$ by aerosol particles (Reactions R1b, R1c) may recycle $ClONO_2$ to more photolabile species (HOCl or Cl_2) and thus amplify the impact of Cl atoms on tropospheric oxidation capacity (Finlayson-Pitts et al., 1989; Deiber et al., 2004). Considering the widespread occurrence of reactive chlorine species (Simpson et al., 2015) and mineral dust particles (Textor et al., 2006; Ginoux et al., 2012; Tang et al., 2016) in the troposphere, our laboratory measurements can also have strong implications for tropospheric chemistry.

Using the UKCA (United Kingdom Chemistry and Aerosol) chemistry–climate model, a preliminary assessment of the effect of injecting TiO_2 into the stratosphere on stratospheric chemistry and ozone was discussed in our previous work (Tang et al., 2014c). This model has also been used to investigate stratospheric ozone change due to volcanic sulfuric acid particles after the eruption of Mt Pinatubo in 1991 (Telford et al., 2009). In the previous work (Tang et al., 2014c), we used the UKCA model to construct a case study in which TiO_2 aerosols were distributed in the stratosphere in a similar way to the volcanic sulfuric acid particles after the eruption of Mt Pinatubo so that the solar-radiation scattering effect was similar for the two scenarios; however, the only heterogeneous reaction on TiO_2 particles considered was the uptake of N_2O_5 (Reaction R1a). Injection of solid aerosols into the stratosphere can have a significant impact on ozone mixing ratios when heterogeneous reactions involving chlorine are considered (Weisenstein et al., 2015). Several previous studies (Jackman et al., 1998; Danilin et al., 2001; Weisenstein et al., 2015) have considered the effects of solid alumina particles on stratospheric chemistry; however, there is only very limited assessment of other potential solid aerosol compositions (e.g. TiO_2 and diamond) (Tang et al., 2014c). Here we expand upon the previous literature by considering in our model a number of heterogeneous reactions with new kinetic data on TiO_2. In our current work the heterogeneous hydrolysis of $ClONO_2$ on TiO_2 particles (Reaction R1b) has been included, using our new experimental data. The changes in stratospheric ozone and reactive nitrogen and chlorine species are assessed by comparing to the impact of the Mt Pinatubo eruption.

2 Experimental section

The heterogeneous reaction of $ClONO_2$ with aerosol particles was investigated at different RHs using an atmospheric pressure aerosol flow tube (AFT). In addition, its uptake onto Pyrex glass was also studied, using a coated-wall flow tube. N_2 was used as a carrier gas, and all the experiments were carried out at 296 ± 2 K.

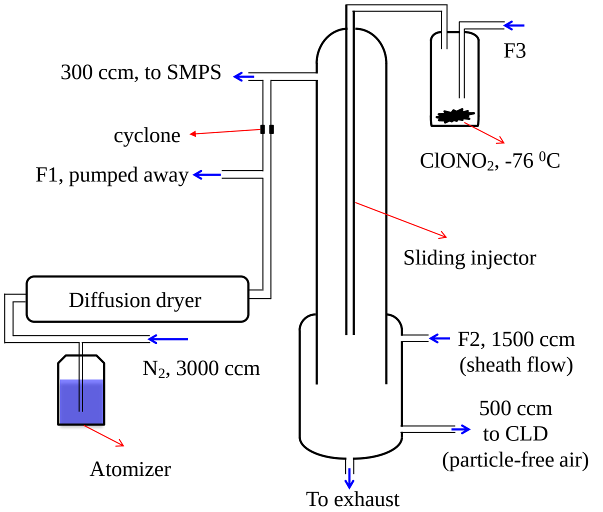


Figure 1. Schematic diagram of the aerosol flow tube used in this study. SMPS: scanning mobility particle sizer; CLD: chemiluminescence detector, used to measure the $ClONO_2$ concentration (measured as the change in NO concentration). All the flows (except the flow applied to the atomiser) were controlled by mass flow controllers. Flow details are provided in the text.

2.1 Aerosol flow tube

2.1.1 Flow tube

A detailed description of the AFT was given in our previous work (Tang et al., 2014a, c), and only the key features are described here. The flow tube, as shown in Fig. 1, is a horizontally mounted Pyrex glass tube (ID: 3.0 cm; length: 100 cm). The total flow in the AFT was 1500 $mL\,min^{-1}$, leading to a linear flow velocity of 3.54 $cm\,s^{-1}$ and a maximum residence time of ∼ 30 s. The Reynolds number is calculated to be 69, suggesting a laminar flow condition in the flow tube. Under our experimental conditions, the entrance length needed to develop the laminar flow is ∼ 12 cm. The mixing length is calculated to be ∼ 14 cm, using a diffusion coefficient of 0.12 $cm^2\,s^{-1}$ for $ClONO_2$ in N_2 at 296 K (Tang et al., 2014b). Only the middle part of the flow tube (30–80 cm) was used to measure the uptake kinetics.

A commercial atomiser (Model 3076, TSI, USA) was used to generate an ensemble of mineral aerosols. N_2 at ∼ 3 bar was applied to the atomiser to disperse the mineral–water mixture (with a TiO_2 or SiO_2 mass fraction of ∼ 0.5 %), resulting in an aerosol flow of 3000 $mL\,min^{-1}$. The aerosol flow was delivered through two diffusion dryers, and the resulting RH was adjusted by varying the amount of silica gel in the diffusion dryers. A flow of 1200 $mL\,min^{-1}$ was pumped away through F1, and the remaining flow (1800 $mL\,min^{-1}$) was then delivered through a cyclone (TSI, USA) to remove super-micrometre particles. This cyclone has a cut-off size of 800 nm at a flow rate of 1000 $mL\,min^{-1}$. The aerosol flow could be delivered through a filter to remove all the particles (to measure the wall loss rate), or alternatively the filter could be bypassed to introduce aerosol particles into the AFT (to measure the total loss rate). Beyond that point, 300 mL min^{-1} was sampled by a scanning mobility particle sizer (SMPS), and the remaining 1500 mL min^{-1} flow was delivered into the AFT via the side arm. Mineral aerosols were characterised online using a SMPS, consisting of a differential mobility analyser (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3775) which was operated with a sampling flow rate of 300 mL min^{-1}. The sheath flow of the DMA was set to 2000 mL min^{-1}, giving a detectable mobility size range of 19–882 nm. The time resolution of the SMPS measurement was 150 s.

The bottom 30 cm of the AFT was coaxially inserted into another Pyrex tube (inner diameter: 4.3 cm; length: 60 cm). A sheath flow (F2, 1500 mL min^{-1}) was delivered through the annular space between the two coaxial tubes. The sheath flow has the same linear velocity as the aerosol flow to minimise the turbulence at the end of the aerosol flow tube where the two flows joined. Gases could exchange between the sheath flow and the aerosol flow because of their large diffusion coefficients (~ 0.1 cm^2 s^{-1}) (Tang et al., 2014b), while aerosol particles remained in the centre due to their much smaller diffusion coefficients, i.e. 10^{-7}–10^{-6} cm^2 s^{-1} (Hinds, 1996). At the end of the large Pyrex tube, a flow of 500 mL min^{-1} was sampled through a 1/4 in. fluorinated ethylene propylene (FEP) tube which intruded 1–2 mm into the flow close to the wall of the Pyrex tube. This gas–particle separation method enabled particle-free gas to be sampled, despite very high aerosol concentrations used in the AFT. Sampling particle-free gas prevents particles from deposition onto the inner wall of the sampling tube and therefore minimises the undesired loss of the reactive trace gases (e.g. $ClONO_2$ in this study) during their transport to the detector. More detailed discussion of this gas–particle separation method used in the aerosol flow experiments is provided elsewhere (Rouviere et al., 2010; Tang et al., 2012).

2.1.2 $ClONO_2$ synthesis

$ClONO_2$ was synthesised in the lab by reacting Cl_2O with N_2O_5 (Davidson et al., 1987; Fernandez et al., 2005). N_2O_5 crystals were synthesised by trapping the product formed from mixing NO with O_3 in large excess (Fahey et al., 1985). The synthesis and purification are detailed in our previous study (Tang et al., 2014c). Cl_2O was synthesised by reacting HgO with Cl_2 (Renard and Bolker, 1976; Molina et al., 1977). Cl_2 from a lecture bottle was first trapped as yellow-green liquid (a few millilitres) in a glass vial at −76 °C using an ethanol–dry-ice bath. It was then warmed up to room temperature so that all the Cl_2 was evaporated and transferred to the second glass vessel, which contained HgO powders in excess and was kept at −76 °C. The glass vessel containing liquid Cl_2 and HgO powders was sealed and kept at −76 °C overnight. It was then warmed up to room temperature to evaporate and transfer the formed Cl_2O and any remaining Cl_2 to the third glass vial kept at −76 °C. Liquid Cl_2O appeared dark reddish-brown in colour.

The third vessel containing Cl_2O was warmed up to room temperature to evaporate and transfer Cl_2O to the fourth vial, which contained synthesised N_2O_5 and was kept at −76 °C. The vial containing Cl_2O and N_2O_5 was sealed and kept at −50 °C for 2–3 days in a cryostat. In this work Cl_2O was in slight excess compared to N_2O_5, and thus all the white powder (solid N_2O_5) was consumed. $ClONO_2$ is liquid at −50 °C, with a colour similar to liquid Cl_2. The major impurity of our synthesised $ClONO_2$ was Cl_2O, and the boiling temperature at 760 torr is 2 °C for Cl_2O and ~ 22 °C for $ClONO_2$ (Stull, 1947; Renard and Bolker, 1976). To purify our synthesised $ClONO_2$, the vial containing $ClONO_2$ was warmed up to 5 °C and connected to a small dry-N_2 flow via a T-piece for a few hours. Note that the N_2 flow was not delivered into the vial but instead served as a dry atmosphere at ~ 760 torr. Cl_2O was boiled at 5 °C and diffused passively into the N_2 flow. Cl_2 was also removed because its boiling temperature is −34 °C (Stull, 1947). The amount of N_2O_5 in $ClONO_2$ was minimised because Cl_2O was in excess. In addition, the vapour pressure (a few millitorr) of N_2O_5 (Stull, 1947) is > 100 times lower than that of $ClONO_2$ (~ 1 torr) at around −76 °C (Schack and Lindahl, 1967; Ballard et al., 1988; Anderson and Fahey, 1990); therefore, even if N_2O_5 were present in the gas phase, its amount would be negligible compared to $ClONO_2$.

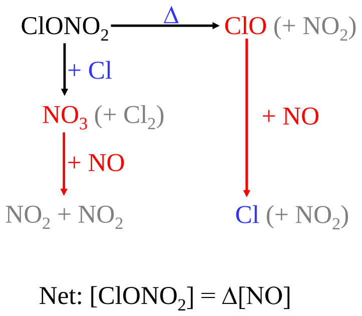
2.1.3 $ClONO_2$ detection

The $ClONO_2$ vial was stored at −76 °C in the dark using a cryostat. A small dry-N_2 flow (a few millilitres per minute, F3) was delivered into the vial to elute gaseous $ClONO_2$. The $ClONO_2$ flow was delivered through 1/8 in. FEP tubing in a stainless-steel injector into the centre of the aerosol flow tube. The position of the injector could be adjusted to vary the interaction time of $ClONO_2$ with aerosols in the flow tube.

The flow sampled from the flow tube (500 mL min^{-1}) was mixed with ~ 5 mL min^{-1} NO (100 ppmv in N_2) and then delivered into a glass reactor heated to 130 °C. The initial NO mixing ratio (in the absence of $ClONO_2$) in the reactor was ~ 1000 ppbv (or $\sim 1.8 \times 10^{13}$ molecule cm^{-3}). The volume of the glass reactor (inner diameter: 2.0 cm; length: 10 cm) is ~ 30 cm^3, corresponding to an average residence time of ~ 2.6 s at 130 °C. The scheme used in our work to detect $ClONO_2$ is shown in scheme 1 and explained in detail below. $ClONO_2$ was thermally decomposed in the reactor to ClO and NO_2 (Reaction R2, where M is the third molecule, e.g. N_2), and ClO was then titrated by NO in excess (Reaction R3):

$$ClONO_2 + M \rightarrow ClO + NO_2 + M, \tag{R2}$$

$$ClO + NO \rightarrow Cl + NO_2. \tag{R3}$$



Scheme 1. The $ClONO_2$ detection scheme used in our work.

Cl atoms produced in Reaction (R3) further reacted with $ClONO_2$ (Reaction R4), and the NO_3 radicals formed were titrated by NO (Reaction R5):

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3, \quad \text{(R4)}$$

$$NO_3 + NO \rightarrow NO_2 + NO_2. \quad \text{(R5)}$$

If the thermal dissociation of $ClONO_2$ (Reaction R2) and the scavenging of ClO and NO_3 radicals by NO (Reactions R3, R4) all reach completion, the initial mixing ratio of $ClONO_2$ is equal to the decrease in the NO mixing ratios before and after introducing $ClONO_2$ into the reactor (Anderson and Fahey, 1990).

The lifetime of $ClONO_2$ with respect to thermal dissociation (Reaction R2) at 130 °C was estimated to be ~ 0.2 s at 160 torr (Anderson and Fahey, 1990), and further increase in pressure to ~ 760 torr would increase the decomposition rate and reduce its lifetime. The lifetime of $ClONO_2$ with respect to Reaction (R4) is not critical for our purpose, although it enhances the overall decay of $ClONO_2$ in the reactor. The second-order rate constants are 1.3×10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of ClO with NO and 2.3×10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of NO_3 with NO at 130 °C (Burkholder et al., 2015), giving lifetimes of $\sim 4 \times 10^{-3}$ s for ClO with respect to Reaction (R3) and $\sim 2 \times 10^{-3}$ s for NO_3 with respect to Reaction (R5) in the presence of $\sim$ 1000 ppbv NO in the reactor. To conclude, under our experimental conditions, the residence time of the gas flow in the heated reactor was long enough for the completion of thermal dissociation of $ClONO_2$ (Reaction R2) and titrations of ClO and NO_3 by NO (Reactions R3 and R5).

The flow exiting the reactor was sampled by a chemiluminescence-based NO_x analyser (Model 200E, Teledyne Instruments, USA), which has a sampling flow rate of 500 mL min^{-1} (±10 %). This instrument has two modes. In the first mode NO is measured by detecting the chemiluminescence of exited NO_2 (NO_2^*) produced by reacting NO with O_3 in excess. The gas flow can also be passed through a convertor cartridge filled with molybdenum (Mo) chips heated to 315 °C, and all the NO_2 (and very likely also some of other NO_y, e.g. HONO, HNO_3) is converted to NO; in this mode the total NO (initial NO, NO converted from NO_2 etc.) is measured and termed NO_x. The two modes are periodically switched, and the instrument has a detection limit of 0.5 ppbv with a time resolution of 1 min.

The response of measured NO and NO_x mixing ratios to the introduction of $ClONO_2$ into the AFT is displayed in Fig. 2. Both the sheath flow and the flow in the AFT were set to 1500 mL min^{-1} (dry N_2), and the injector was at 40 cm. The introduction of $ClONO_2$ into the AFT at $\sim$ 20 min leads to the decrease of NO (solid curve in Fig. 2a) from $\sim$ 1100 to $\sim$ 400 ppbv, and NO recovered to its initial level after stopping the $ClONO_2$ flow at $\sim$ 120 min. The $ClONO_2$ mixing ratio (solid curve in Fig. 2b), derived from the change in the NO mixing ratio, was very stable over 100 min. As expected, the introduction of $ClONO_2$ into the system led to the increase of the measured NO_x mixing ratio (dashed curve in Fig. 2a). Ideally the increase in NO_x mixing ratios due to the introduction of $ClONO_2$ should be equal to the $ClONO_2$ mixing ratio. The nitrogen balance (dashed curve in Fig. 2b), defined as the difference in the $ClONO_2$ mixing ratios (equal to the change in NO mixing ratios) and the change of the NO_x mixing ratios, is essentially zero within the experimental noise level. This gives us further confidence in the purity of our synthesised $ClONO_2$: under our current detection scheme the change in the NO_x mixing ratios will be twice that of the N_2O_5 mixing ratio, and therefore N_2O_5 contained in the $ClONO_2$ flow as an impurity was negligible. This method provides a simple and relatively selective method to quantify $ClONO_2$, and it could be used to calibrate other $ClONO_2$ detection methods (Anderson and Fahey, 1990). One previous study used a similar method to detect $ClONO_2$ in its experiments of $ClONO_2$ uptake onto sulfuric acid aerosol particles (Ball et al., 1998), with the only difference being that in that study NO was detected by its absorption at 1845.5135 cm^{-1}. Their reported $\gamma(ClONO_2)$ onto sulfuric acid aerosol particles are in good agreement with those measured by other studies in which $ClONO_2$ was measured using mass spectrometry. This suggests that the indirect detection method of $ClONO_2$ utilised by Ball et al. (1998) and in this work can be used to investigate the uptake of $ClONO_2$ onto aerosol particles.

2.2 Coated-wall flow tube

The coated-wall flow tube, a Pyrex glass tube with an inner diameter of 30 mm, was used to measure the uptake of $ClONO_2$ onto fresh Pyrex glass. The inner wall was rinsed with diluted NaOH solution and then by methanol and deionised water. A flow of 1500 mL min^{-1}, humidified to the desired RH, was delivered into the top of the flow tube via a side arm. A small N_2 flow was used to elute the liquid $ClONO_2$ sample, and the flow was then delivered through a 1/8 in. Teflon tube in a stainless-steel injector into the centre of the flow tube. The position of the injector could be changed to vary the interaction time between $ClONO_2$ and the inner wall of the flow tube. At the bottom of the flow

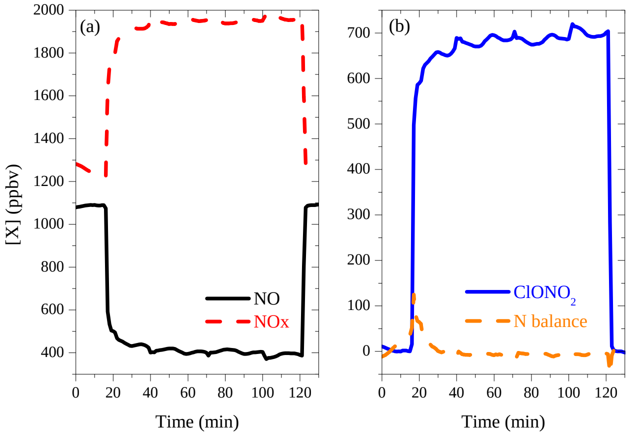


Figure 2. Response of measured NO and NO_x mixing ratios to the introduction of $ClONO_2$ into the flow tube (left panel). The corresponding calculated $ClONO_2$ mixing ratio and nitrogen balance are also shown (right panel).

tube, a flow of 500 mL min^{-1} was sampled through another side arm, mixed with ~ 5 mL min^{-1} NO (100 ppmv in N_2) and then delivered into a glass reactor heated to 130 °C. The flow exiting the heated glass reactor was then sampled into a NO_x analyser. The method used to detect $ClONO_2$ is detailed in Sect. 2.1. The remaining flow (~ 1000 mL min^{-1}) went through a RH sensor into the exhaust.

The linear flow velocity in the flow tube is 3.54 cm s^{-1} with a Reynolds number of 69, suggesting that the flow is laminar. The length of the flow tube, defined as the distance between the side arm through which the main flow was delivered into the flow tube and the other side arm through which 500 mL min^{-1} was sampled from the flow tube into the NO_x analyser, is 100 cm, giving a maximum residence time of ~ 30 s. The entrance length required to fully develop the laminar flow and the mixing length required to fully mix $ClONO_2$ with the main flow are both less than 15 cm. The loss of $ClONO_2$ onto the inner wall was measured using the middle part (30–80 cm) of the flow tube.

2.3 Chemicals

NO (> 99 % purity) in a lecture bottle and the 100 ppmv (±1 ppmv) of NO in N_2 were supplied by CK Special Gas (UK). Pure Cl_2 (with a purity of > 99.5 %) in a lecture bottle and HgO (yellow powder, with a purity of > 99 %) were provided by Sigma-Aldrich (UK). N_2 and O_2 were provided by BOC Industrial Gases (UK). P25 TiO_2, with an anatase-to-rutile ratio of 3 : 1, was supplied by Degussa-Hüls AG (Germany). SiO_2 powders with a stated average particle size (aggregate) of 200–300 nm were purchased from Sigma-Aldrich (UK). The Brunauer–Emmett–Teller (BET) surface area is 8.3 m^2 g^{-1} for TiO_2 (Tang et al., 2014c) and ~ 201 m^2 g^{-1} for SiO_2 (Tang et al., 2014a).

3 Model description

The UKCA chemistry–climate model in its coupled stratosphere–troposphere configuration, which combines both the tropospheric (O'Connor et al., 2014) and stratospheric (Morgenstern et al., 2009) schemes, was used to simulate the effect of heterogeneous hydrolysis of N_2O_5 (Reaction R1a) and $ClONO_2$ (Reaction R1b) on TiO_2. In this model the chemical cycles of O_x, HO_x and NO_x; the oxidation of CO, ethane, propane and isoprene; and chlorine and bromine chemistry are all included. The model also includes a detailed treatment of polar processes. UKCA uses an equilibrium scheme to determine the presence and abundance of nitric acid trihydrate (NAT) and ice PSCs, assuming thermodynamic equilibrium with gas-phase HNO_3 and water vapour (Chipperfield, 1999). Chlorine activation through heterogeneous reactions occurs on both PSC particles and sulfuric acid aerosols (Morgenstern et al., 2009).

The same approach used to investigate the effects of the eruption of Mt Pinatubo on stratospheric ozone (Telford et al., 2009) is adopted in this study. Using the UKCA model in a "nudged" configuration, Telford et al. (2009) evaluated the difference of stratospheric ozone with and without the additional sulfuric acid aerosols caused by the eruption of Mt Pinatubo. "Nudging", or Newtonian relaxation, is a method that provides a realistic representation of short-term dynamical features by adjusting modelled dynamical variables towards meteorological reanalysis data. This process was detailed by a previous study (Telford et al., 2008) and has been used in a number of other models (Jeuken et al., 1996; Takemura et al., 2000; Hauglustaine et al., 2004; Schmidt et al., 2006). By constraining the dynamics of the model in this way, the model is able to faithfully reproduce the meteorology of the time period around the eruption of Mt Pinatubo.

In our current study three simulations are used to assess the effects of TiO_2 particle injection into the stratosphere. All three simulations are started from a spun-up initial condition and run from December 1990 to January 1993. In the base scenario (S1), an aerosol climatology is used which represents the background loading of stratospheric sulfate aerosol. Alongside S1 two further simulations were performed, one representing the eruption of Mt Pinatubo in June 1991 (S2) and a second (S3) in which the Mt Pinatubo eruption is replaced with a single injection of TiO_2 particles on the same date. The simulations are set up so that the radiative impacts at the surface are comparable between S2 and S3. Pope et al. (2012) have proposed that 10 Tg of TiO_2 aerosol particles with an assumed radius of 70 nm are required in order to achieve the same solar-radiation scattering effect as the eruption of Mt Pinatubo. The total surface area of TiO_2 is calculated from the mass of TiO_2 particles, using a density of 4.23 g cm^{-3} and an assumed radius of 70 nm, and the global distribution of TiO_2 is scaled to the sulfuric acid aerosol distribution resulting from the eruption of Mt Pinatubo. The sulfuric acid aerosol surface area distribution was derived

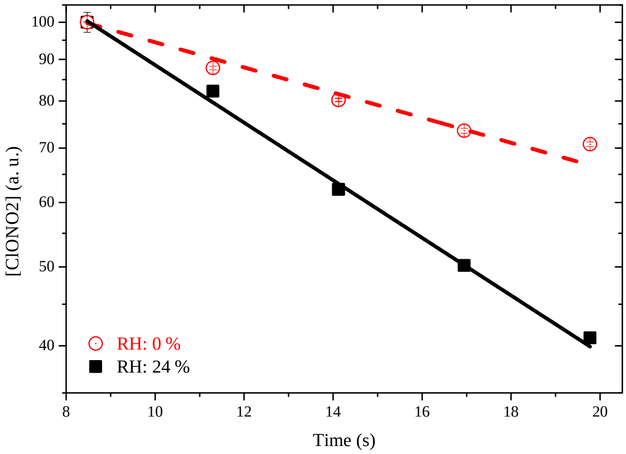


Figure 3. Decays of $ClONO_2$ in the flow tube due to its loss onto the Pyrex glass (circles: 0 % RH; squares: 24 % RH). Measured $ClONO_2$ mixing ratios were normalised to that at 8.5 s (when the injector was at 30 cm). Typical $ClONO_2$ mixing ratios in the flow tube are a few hundred parts per billion by volume (ppbv; see Fig. 2).

from the Stratosphere–troposphere Processes And their Role in Climate (SPARC) climatology (SPARC, 2006).

By running these three scenarios, we are able to compare the relative impact of stratospheric particle injection using TiO_2 compared to sulfate. The benefit of using the Mt Pinatubo eruption as the sulfate injection scenario is that it provides a natural analogue to proposed climate engineering schemes, and the chemical and dynamical effects of the eruption have been well documented. Telford et al. (2009) have shown that UKCA accurately models the chemical impacts of the Mt Pinatubo eruption, and the ozone bias is smaller now than in Telford et al. (2009).

It should be noted that all simulations are nudged to the same observed meteorological conditions, following Telford et al. (2008). In this way we do not take into account the radiative/dynamical feedbacks from any ozone changes resulting from chemical reactions occurring on stratospheric aerosols, allowing just the chemical effects of stratospheric particle injection to be quantified. The results presented here expand on our previous study (Tang et al., 2014c) by including heterogeneous hydrolysis of both N_2O_5 (Reaction R1a) and $ClONO_2$ (Reaction R1b) on TiO_2. An uptake coefficient of 1.5×10^{-3} is used for Reaction (R1a) (reaction with N_2O_5) on TiO_2 particles as determined by our previous measurement (Tang et al., 2014c). An uptake coefficient of 1.5×10^{-3} is used for Reaction (R1b) (heterogeneous hydrolysis of $ClONO_2$). Considering errors in measurements, this value agrees with experimental $\gamma(ClONO_2)$, which was determined to be $\sim 1.2 \times 10^{-3}$ in our work as shown in Table 2.

Table 1. Loss rates (k_w), effective uptake coefficients (γ_eff) and true uptake coefficients (γ) of $ClONO_2$ onto the inner wall of the Pyrex tube at different relative humidities (RHs). Measurements were all carried out with initial $ClONO_2$ mixing ratios of several hundred ppbv.

RH (%)	k_w ($\times 10^{-2}$ s^{-1})	γ_eff ($\times 10^{-6}$)	γ ($\times 10^{-6}$)
0	3.6 ± 0.2	4.2 ± 0.3	5.1 ± 0.3
	2.9 ± 0.4	3.4 ± 0.5	3.9 ± 0.6
6	4.1 ± 0.1	4.9 ± 0.1	6.2 ± 0.1
	3.7 ± 0.7	4.4 ± 0.8	5.4 ± 1.0
12	4.1 ± 0.3	4.9 ± 0.4	6.2 ± 0.5
17	6.9 ± 0.3	8.2 ± 0.4	13 ± 0.6
	6.4 ± 0.2	7.6 ± 0.2	11 ± 0.4
24	8.1 ± 0.8	9.6 ± 1.0	16 ± 2.0
	8.2 ± 0.3	9.6 ± 0.4	17 ± 0.7

4 Results and discussion

4.1 Uptake of $ClONO_2$ onto Pyrex glass

The uptake of $ClONO_2$ onto a fresh Pyrex glass wall was determined by measuring the $ClONO_2$ concentrations at five different injection positions. The loss of $ClONO_2$ in the coated-wall flow tube, under the assumption of pseudo-first-order kinetics, can be described by Eq. (1):

$$[ClONO_2]_t = [ClONO_2]_0 \cdot \exp(-k_\mathrm{w} \cdot t), \tag{1}$$

where $[ClONO_2]_t$ and $[ClONO_2]_0$ are the measured $ClONO_2$ concentrations at the reaction time of t and 0, respectively, and k_w is the wall loss rate (s^{-1}). Two typical datasets of measured $[ClONO_2]$ at five different injector positions are displayed in Fig. 3, suggesting that $ClONO_2$ indeed follows the exponential decays, and the slopes of the exponential decays are equal to k_w. The effective (or experimental) uptake coefficient of $ClONO_2$, γ_eff, onto the Pyrex wall can then be calculated from k_w, using Eq. (2) (Howard, 1979; Wagner et al., 2008):

$$\gamma_\mathrm{eff} = \frac{k_\mathrm{w} \cdot d_\mathrm{tube}}{c(ClONO_2)}, \tag{2}$$

where d_tube is the inner diameter of the flow tube (3.0 cm) and $c(ClONO_2)$ is the average molecular speed of $ClONO_2$ (25 360 cm s^{-1}). Depletion of $ClONO_2$ close to the wall is caused by the uptake of $ClONO_2$ onto the wall, and thus the effective uptake coefficient is smaller than the true one. This effect can be corrected (Tang et al., 2014b), and true uptake coefficients, γ, are reported in Table 1 together with the corresponding wall loss rates (k_w) and effective uptake coefficients (γ_eff).

The uptake coefficients of $ClONO_2$ onto Pyrex glass, as summarised in Table 1, increases from $\sim 5 \times 10^{-6}$ at 0 % RH to $\sim 1.6 \times 10^{-5}$ at 24 % RH by a factor of ~ 3. Uptake coefficients at higher RH were not determined because the uptake coefficients determined at 24 % RH ($\sim 1.6 \times 10^{-5}$) are very close to the upper limit ($\sim 2.3 \times 10^{-5}$), which can be measured in this study using the coated-wall flow tube technique due to the gas-phase diffusion limit. The RH dependence of $\gamma(ClONO_2)$ for Pyrex glass is further discussed in Sect. 4.4 together with those reported by Molina et al. (1997) and our measurements on SiO_2 and TiO_2 aerosol particles.

4.2 Reaction of $ClONO_2$ with SiO_2 and TiO_2 particles

The uptake of $ClONO_2$ onto airborne SiO_2 and TiO_2 particles was investigated using an atmospheric pressure aerosol flow tube, in which reactions with the aerosol particles and the wall both contribute to the loss of $ClONO_2$, as shown in Eq. (3):

$$[ClONO_2]_t = [ClONO_2]_0 \cdot \exp[-(k_w + k_a) \cdot t], \quad (3)$$

where $[ClONO_2]_t$ and $[ClONO_2]_0$ are the measured $ClONO_2$ mixing ratios at the reaction times of t and 0 s, and k_w and k_a are the loss rates (s^{-1}) of $ClONO_2$ onto the inner wall of the flow tube and the surface of aerosol particles, respectively. In a typical uptake measurement, the aerosol flow was delivered through a filter, and $[ClONO_2]$ was measured at five different injector positions to determine the wall loss rate (k_w). The filter was then bypassed to deliver aerosol particles into the flow tube, and the total $ClONO_2$ loss rate ($k_w + k_a$) in the flow tube was determined. After that, the aerosol flow was passed through the filter to measure k_w again. The variation of k_w determined before and after introducing particles into the flow tube was within the experimental uncertainty of k_w, ensuring that the reactivity of the wall towards $ClONO_2$ remained constant during the uptake measurement. Axial and radical diffusion of $ClONO_2$ could lead to biases in its measured loss rates in a flow tube, and this effect, though very small ($< 10\,\%$ in our work), has been corrected (Brown, 1978).

The difference between the $ClONO_2$ loss rates without and with aerosol particles in the flow tube is equal to the loss rate due to the reaction with the surface of aerosol particles (k_a). The effective uptake coefficient of $ClONO_2$ onto aerosol particles, γ_{eff}, is related to k_a by Eq. (4) (Crowley et al., 2010):

$$k_a = 0.25 \cdot \gamma_{eff} \cdot c\,(ClONO_2) \cdot S_a, \quad (4)$$

where S_a is the aerosol surface area concentration which can be derived from size-resolved number concentrations (as shown in Fig. S1 in the Supplement) measured by the SMPS. Uptake of $ClONO_2$ onto aerosol particles also leads to the depletion of $ClONO_2$ near the particle surface, and so the effective uptake coefficient is smaller than the true uptake coefficient. This effect, which can be corrected using the method described elsewhere (Tang et al., 2014b), is only a few percent in this study as the particle diameters are < 1 µm and the uptake coefficient is relatively small ($\sim 1 \times 10^{-3}$).

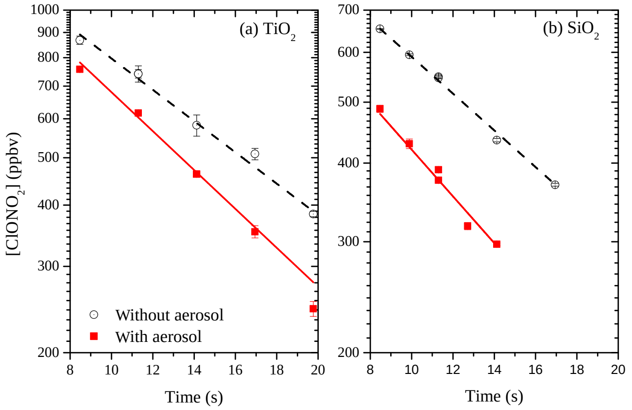


Figure 4. Decays of $ClONO_2$ in the aerosol flow tube without (open circles) and with (solid squares) aerosol particles in the aerosol flow tube under different experimental conditions. **(a)** TiO_2 with a surface area concentration of 2.3×10^{-3} cm^2 cm^{-3} at 33 % RH; **(b)** SiO_2 with a surface area concentration of 2.9×10^{-3} cm^2 cm^{-3} at 39 % RH.

Two typical decays of $ClONO_2$ in the aerosol flow tube without and with SiO_2/TiO_2 aerosol particles in the flow tube are shown in Fig. 4. For a majority of experiments, efforts were made to generate enough aerosol particles so that $k_a + k_w$ was significantly different to k_w. It is evident from Fig. 4 that the loss of $ClONO_2$ is significantly faster with TiO_2/SiO_2 particles in the flow tube than without aerosols. We acknowledge that the measured k_a and therefore our reported γ in this study have quite large uncertainties. This is because the uptake coefficients of $ClONO_2$ are very small and the surface area of the wall is ~ 1000 times larger than that of aerosol particles. This is the first time that heterogeneous reactions of $ClONO_2$ with airborne mineral particles have been investigated.

The uptake coefficients of $ClONO_2$ are $\sim 1.2 \times 10^{-3}$ for TiO_2 particles, and no difference in $\gamma(ClONO_2)$ at two different RHs (7 and 33 %) is found. The heterogeneous reaction of $ClONO_2$ with SiO_2 particles was studied at four different RHs, with $\gamma(ClONO_2)$ increasing from $\sim 2 \times 10^{-4}$ at 7 % RH to $\sim 5 \times 10^{-4}$ at 35 % RH, reaching a value of $\sim 6 \times 10^{-4}$ at 59 % RH. The uptake coefficients of $ClONO_2$ are summarised in Table 2 for SiO_2 and TiO_2 aerosol particles, together with key experimental conditions. It should be pointed out that our measurements were carried out with $ClONO_2$ mixing ratios of several hundred parts per billion by volume (ppbv), significantly higher than those found in the lower stratosphere. Therefore, our measurements could underestimate $\gamma(ClONO_2)$ under stratospheric conditions. In a few measurements in which the SiO_2 aerosol concentrations were relatively low, the total $ClONO_2$ loss rate ($k_w + k_a$) was not different from its wall loss rate (k_w) within the experimental uncertainty. In this case, only the upper limit of k_a (and thus γ) can be estimated, which is reported here as the standard deviation of k_w. The first three of the four uptake coefficients at (17 ± 2) % RH for SiO_2 aerosol particles, tabulated in Table 2, fall into this category. $\gamma(ClONO_2)$ on SiO_2

Table 2. Uptake coefficients of $ClONO_2$ onto SiO_2 and TiO_2 aerosol particles at different RHs. k_a: loss rate of $ClONO_2$ onto aerosol particle surface; S_a: aerosol surface area concentration; $\gamma(ClONO_2)$: uptake coefficients of $ClONO_2$. Measurements were all carried out with initial $ClONO_2$ mixing ratios of several hundred ppbv.

Particle	RH (%)	k_a ($\times 10^{-3}$ s)	S_a ($\times 10^{-3}$ cm^2 cm^{-3})	$\gamma(ClONO_2)$ ($\times 10^{-4}$)
SiO_2	7 ± 1	4.1 ± 2.5	2.80 ± 0.02	2.3 ± 1.4
	7 ± 1	3.4 ± 3.2	2.78 ± 0.05	1.9 ± 1.8
	17 ± 2	< 5.1*	1.08 ± 0.08	< 7.5*
	17 ± 2	< 5.4*	1.28 ± 0.07	< 6.7*
	17 ± 2	< 7.3*	1.78 ± 0.09	< 6.5*
	17 ± 2	6.5 ± 4.2	2.08 ± 0.06	4.9 ± 3.2
	35 ± 4	6.3 ± 3.1	2.34 ± 0.08	4.2 ± 2.1
	35 ± 4	13.1 ± 4.7	2.91 ± 0.09	7.1 ± 2.6
	35 ± 4	9.0 ± 7.3	2.86 ± 0.10	4.8 ± 3.9
	59 ± 3	11.6 ± 3.5	2.88 ± 0.06	6.4 ± 1.9
TiO_2	7 ± 1	7.0 ± 1.4	1.09 ± 0.12	10.1 ± 2.0
	7 ± 1	6.2 ± 2.3	0.73 ± 0.05	13.7 ± 5.0
	33 ± 3	17.9 ± 5.6	2.23 ± 0.03	12.7 ± 3.9
	33 ± 3	14.5 ± 1.4	1.93 ± 0.03	11.9 ± 1.1

* Estimated upper limits.

aerosol particles is around 2 orders of magnitude larger than that on Pyrex glass. One explanation for such a large difference is that SiO_2 particles used in our work are porous (Tang et al., 2014a), and therefore the surface area which is actually available for the $ClONO_2$ uptake is much larger than that calculated using the mobility diameters. In our previous study (Tang et al., 2014a) we have found that, for SiO_2 particles, $\gamma(N_2O_5)$ calculated using the mobility-diameter-based surface area are a factor of 40 larger than those calculated using the BET surface area. Another reason is that the composition of SiO_2 is different from Pyrex.

4.3 Effects of RH

The RH dependence of $\gamma(ClONO_2)$ for Pyrex glass is plotted in Fig. 5 and exhibits a positive dependence on RH, with $\gamma(ClONO_2)$ increased by a factor of ∼ 3 when RH increases from 0 to 24 %. Previous studies (Hanson and Ravishankara, 1991, 1994; Zhang et al., 1994; Hanson, 1998) have shown that $\gamma(ClONO_2)$ for aqueous H_2SO_4 solution strongly depends on water content in the solution, and it decreases from ∼ 0.1 for 40 % H_2SO_4 to $\sim 1 \times 10^{-4}$ for 75 % H_2SO_4 at 200–200 K, by a factor of ∼ 1000. It is suggested that the heterogeneous uptake of $ClONO_2$ by aqueous H_2SO_4 solution proceeds via direct and acid-catalysed hydrolysis (Robinson et al., 1997; Shi et al., 2001; Ammann et al., 2013). One may expect that $\gamma(ClONO_2)$ for Pyrex glass will increase with RH. This is also supported by the water adsorption isotherm on Pyrex glass particles (Chikazawa et al., 1984), showing that the amount of adsorbed water on the Pyrex surface displays a substantial increase at 20 % RH compared to that at 0 % RH. However, the results reported by Chikazawa et al. (1984) are presented graphically and thus impede us from a more quantitative discussion on the effect of RH and surface-adsorbed water on uptake of $ClONO_2$ by the Pyrex surface.

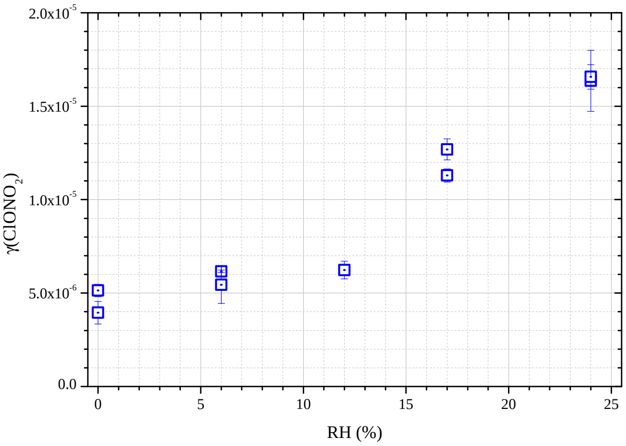


Figure 5. Dependence of $\gamma(ClONO_2)$ on RH for Pyrex glass.

One can then expect that $\gamma(ClONO_2)$ may also increase with RH for the reaction with SiO_2 and TiO_2 aerosol particles, since the amount of water adsorbed on these two types of particles also increases with RH (Goodman et al., 2001). Inspection of the data listed in Table 2 reveals that $\gamma(ClONO_2)$ for SiO_2 particle increases from $\sim 2 \times 10^{-4}$ at 7 % RH to $\sim 6 \times 10^{-4}$ at 59 % RH, and this is consistent with the large increase of adsorbed water on the SiO_2 surface, from around half a monolayer at ∼ 7 % RH to two monolayers at 60 % RH (Goodman et al., 2001), as shown in Fig. S2.

The uptake coefficients of $ClONO_2$ were measured to be $\sim 1.2 \times 10^{-3}$ for TiO_2 at 7 and 33 % RH, with no significant difference found at these two different RHs. We expect that further increase in RH will lead to larger $\gamma(ClONO_2)$ for TiO_2, and future studies at higher RH are needed to better understand the RH effects.

At similar RH (7 and 33 %), $\gamma(ClONO_2)$ for TiO_2 are significantly larger than those for SiO_2. This may be explained by the larger amount of adsorbed water on TiO_2 at low and medium RH than on SiO_2 as shown in Fig. S2. It is interesting to note that the uptake of N_2O_5 shows different behaviour; i.e. $\gamma(N_2O_5)$ for SiO_2 (Tang et al., 2014a) are significantly larger than that for TiO_2 at similar RH. This may indicate that a different mechanism controls N_2O_5 uptake by mineral surfaces. However, mechanistic explanations of the different heterogeneous reactivities of N_2O_5 and $ClONO_2$ on the TiO_2 and SiO_2 surface at the molecular level cannot be derived from our data.

4.4 Comparison with previous work

We find that, in the absence of HCl, $\gamma(ClONO_2)$ is around 1.2×10^{-3} for TiO_2 aerosol particles and $< 1 \times 10^{-3}$ for SiO_2 aerosol particles at room temperature. Using the coated-wall flow tube technique, Molina et al. (1997) investigated the uptake of $ClONO_2$ onto the inner wall of an Al_2O_3 tube, α-Al_2O_3 particles and the inner wall of a Pyrex glass tube, in the presence of (1–10) $\times 10^{-6}$ torr HCl at 200–220 K. Uptake coefficients of ~ 0.02 were reported for all the three types of surface (including Pyrex glass), over a factor of 1000 larger than $\gamma(ClONO_2)$ for Pyrex glass determined in our present work. The large difference in $\gamma(ClONO_2)$ reported by the two studies is likely due to the co-presence of HCl (1×10^{-6}–1×10^{-5} torr) in the experiments of Molina et al. (1997), while no HCl was present in our work. Heterogeneous reactions of $ClONO_2$ proceed via direct and acid-catalysed hydrolysis (Robinson et al., 1997; Shi et al., 2001; Ammann et al., 2013), and numerous previous studies have confirmed that the presence of HCl in the gas phase (and thus partitioning into or adsorption onto the condensed phases) promotes the uptake of $ClONO_2$ by H_2SO_4 solution, ice and NAT, as summarised by Crowley et al. (2010), Burkholder et al. (2015) and Ammann et al. (2013). Temperature may also play a role since measurements were carried out at 200–220 K by Molina et al. (1997) and at ~ 296 K in our study.

Considering the importance of HCl in the $ClONO_2$ uptake and its abundance in the stratosphere, it will be important to systematically measure $\gamma(ClONO_2)$ for SiO_2/TiO_2 in the presence of HCl over a broad HCl concentration and temperature range relevant for the lower stratosphere.

5 Implication for stratospheric particle injection

Injection of TiO_2 into the stratosphere will provide additional surface area for the heterogeneous reactions of N_2O_5 (Reaction R1a) and $ClONO_2$ (Reactions R1b, R1c). There are several important types of particles naturally present in the stratosphere (Solomon, 1999), including sulfuric acid, ice and NAT, and their interaction with $ClONO_2$ has been well characterised (Crowley et al., 2010; Ammann et al., 2013; Burkholder et al., 2015). Comparing $\gamma(ClONO_2)$ for TiO_2 particles with these other stratospherically relevant surfaces can provide a first-order estimate of their relative importance.

The uptake of $ClONO_2$ on H_2SO_4 acid particles is strongly influenced by temperature and the water content in the particles (Shi et al., 2001; Ammann et al., 2013; Burkholder et al., 2015): $\gamma(ClONO_2)$ are $< 2 \times 10^{-3}$ for 65 wt % H_2SO_4 particles and $< 2 \times 10^{-4}$ for 75 wt % H_2SO_4 particles. The global distribution of $\gamma(ClONO_2)$ calculated for sulfuric acid particles in the stratosphere is shown in the Supplement (Fig. S3), suggesting that $\gamma(ClONO_2)$ is lower on TiO_2 particles than on sulfuric acid particles in the lower stratosphere. The uptake coefficient of $ClONO_2$ for water ice shows a negative dependence on temperature, with $\gamma(ClONO_2)$ of ~ 0.1 at ~ 200 K (Crowley et al., 2010; Burkholder et al., 2015), around a factor of 100 larger than that for TiO_2 particles at room temperature. $\gamma(ClONO_2)$ for water-rich nitric acid trihydrate (NAT), another important component for polar stratospheric clouds, increases strongly with temperature, with $\gamma(ClONO_2)$ of 3.0×10^{-3} at 200 K, 6.0×10^{-3} at 210 K and 1.14×10^{-2} at 220 K (Crowley et al., 2010).

While the background burden of stratospheric aerosol is low, volcanic eruptions and deliberate stratospheric particle injection for climate engineering purposes have the potential to significantly increase the available surfaces for heterogeneous reactions. In our current work, three simulations were performed, one representing a low background loading of stratospheric sulfate (< 1 Tg) aerosols (S1), a second representing the eruption of Mt Pinatubo (S2) and a third representing an instantaneous injection of 10 Tg of TiO_2 (S3). SiO_2 particle injection is not considered in our modelling study because the refractive index of SiO_2 is significantly smaller than TiO_2 (Pope et al., 2012). Two heterogeneous reactions on TiO_2 particles, i.e. heterogeneous hydrolysis of N_2O_5 (Reaction R1a) and $ClONO_2$ (Reaction R1b), were included in the simulation: a value of 1.5×10^{-3} was used for $\gamma(N_2O_5)$, as measured in our previous work (Tang et al., 2014c), and $\gamma(ClONO_2)$ was also set to 1.5×10^{-3}, based on the measurement reported in our current study. All three simulations were nudged to observed meteorology from December 1990 to January 1993. By comparing the TiO_2 injection (S3) with the Mt Pinatubo eruption (S2), we are able to quantify the relative impacts of TiO_2 and sulfuric acid injection on stratospheric chemistry. Results in this section are presented as annual means for the year 1992.

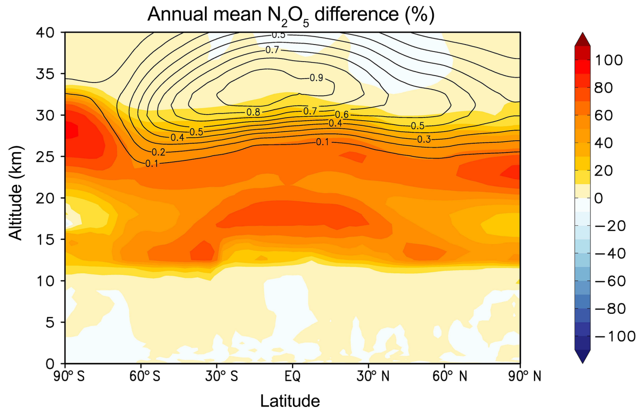


Figure 6. Simulated annual-mean, zonal-mean N_2O_5 percentage differences between TiO_2 injection (S3) and the Mt Pinatubo eruption (S2). Black contour lines show N_2O_5 mixing ratios from the Mt Pinatubo simulation (S2) in ppbv.

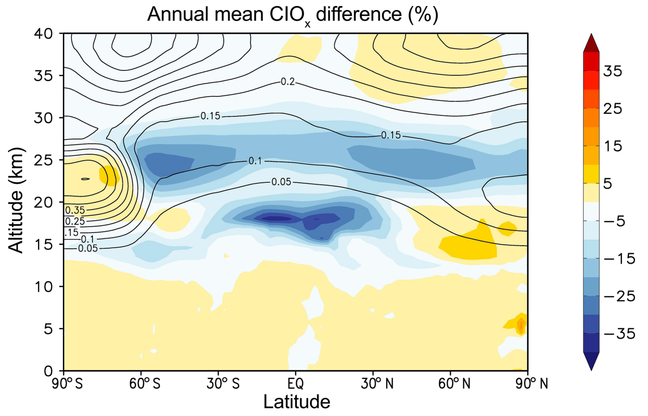


Figure 7. Simulated annual-mean, zonal-mean ClO_x percentage differences between TiO_2 injection (S3) and the Mt Pinatubo eruption (S2). Black contour lines show ClO_x mixing ratios from the Mt Pinatubo simulation (S2) in ppbv.

Similar to our previous study (Tang et al., 2014c), we have found that injection of TiO_2 (S3) has a much smaller impact on stratospheric N_2O_5 concentrations than the eruption of Mt Pinatubo (S2). N_2O_5 mixing ratios are significantly reduced in S2 compared to S1 from 10 to 30 km, with concentrations reduced by $> 80\,\%$ throughout most of this region. For comparison, after TiO_2 injection (S3) N_2O_5 concentrations are reduced over a much smaller altitude range (15–25 km) and to a lesser degree, with $\sim 20\,\%$ reductions in the tropics and up to 60 % reductions in the high latitudes. The relative effects of TiO_2 injection compared to sulfate injection on N_2O_5 mixing ratios is calculated as the difference between S3 and S2. As shown in Fig. 6, throughout most of the stratosphere N_2O_5 mixing ratios remain higher under S3 than S2.

Under both particle injection scenarios (S2 and S3), stratospheric ClO_x mixing ratios are increased compared to S1 due to the activation of $ClONO_2$ through heterogeneous reactions. However, Fig. 7 suggests that ClO_x mixing ratios are up to 40 % lower in the tropical lower stratosphere following the injection of TiO_2 aerosols compared to sulfate. This is driven in part by the lower surface area density of TiO_2 compared to sulfate but is also due to the difference in uptake coefficients. The uptake coefficient of $ClONO_2$ onto sulfate is temperature-dependent, and our measurements suggest that the uptake coefficient onto fresh TiO_2 is smaller than that for sulfate below ~ 215 K. Throughout much of the tropical lower stratosphere where maximum aerosol surface area density is found in both S2 and S3, temperatures are below ~ 220 K, and therefore the uptake coefficient is lower for TiO_2 than sulfate (as shown by Fig. S3 in the Supplement), leading to reduced chlorine activation. Previous studies have investigated the influence of temperature on the heterogeneous reactions of mineral particles with a few other trace gases – including HCOOH (Wu et al., 2012), H_2O_2 (Romanias et al., 2012) and OH radicals (Bedjanian et al., 2013) – and found that the measured uptake coefficients varied only by a factor of 2–3 or less across a wide temperature range. However, it is unclear whether temperature would have a significant effect on $\gamma(ClONO_2)$ for TiO_2 particles, and therefore our simulated impact of heterogeneous reaction of $ClONO_2$ with TiO_2 on stratospheric chemistry may have large uncertainties. The sensitivity of simulated stratospheric compositions to $\gamma(ClONO_2)$ for TiO_2 particles will be investigated in a following paper.

The relative difference in ozone mixing ratios following TiO_2 injection (S3) compared with the eruption of Mt Pinatubo (S2) is shown in Fig. 8. Ozone mixing ratios in the lower stratosphere decrease as a result of both TiO_2 and sulfate injection, with the largest decreases seen at high latitudes. In terms of annual means, the magnitude of this ozone response is comparable between the two simulations, with a maximum of $\sim 3\,\%$ in the tropics and $\sim 7\,\%$ at high latitudes. In contrast, ozone mixing ratios at the altitude of 25 km increase following the eruption of Mt Pinatubo (S2) but show no significant change upon TiO_2 injection (S3). This is consistent with the much faster uptake of N_2O_5 onto sulfate aerosols and the resultant stratospheric NO_x loss and decreases in the rates of catalytic ozone destruction at these altitudes.

The results presented here indicate that there is little difference in stratospheric ozone concentrations between injection of TiO_2 and sulfate aerosols when Reactions (R1a) and (R1b) are considered on TiO_2. While TiO_2 injection (S3) leads to less ClO_x activation and ozone destruction in the lowermost stratosphere, the reduced depletion of N_2O_5 and NO_x in the middle stratosphere leads to decreased ozone mixing ratios compared to sulfate injection (S2). The total column ozone differences between S3 and S2 are within ±2.5 %, indicating that there is no significant difference in vertically integrated

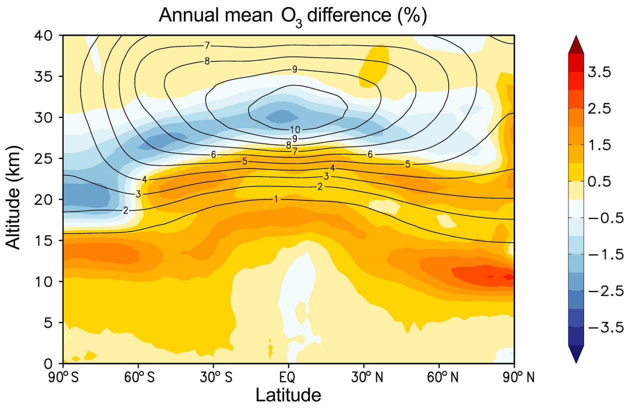


Figure 8. Simulated annual-mean, zonal-mean O_3 percentage differences between TiO_2 injection (S3) and the Mt Pinatubo eruption (S2). Black contour lines show ClO_x mixing ratios from the Mt Pinatubo simulation (S2) in parts per million by volume (ppmv).

ozone abundances and solar UV amounts reaching the surface. However, more work is required to establish additional kinetic data for heterogeneous reactions of TiO_2.

6 Conclusions and outlook

Minerals with high refractive indices, such as TiO_2, have been proposed as possible materials used for stratospheric particle injection for climate engineering (Pope et al., 2012). However, kinetic data of their heterogeneous reactions with important reactive trace gases (e.g. N_2O_5 and $ClONO_2$) in the stratosphere are lacking, impeding us from a reliable assessment of the impacts of mineral particle injection on stratospheric ozone in particular and stratosphere chemistry in general. In our current work, using an atmospheric pressure aerosol flow tube, we have investigated the heterogeneous reaction of $ClONO_2$ with TiO_2 and SiO_2 aerosol particles at room temperature and at different RHs. The uptake coefficient, $\gamma(ClONO_2)$, was $\sim 1.2 \times 10^{-3}$ at 7 and 33 % RH for TiO_2 particles, with no significant difference observed at these two RHs; for SiO_2 particles, $\gamma(ClONO_2)$ increases from $\sim 2 \times 10^{-4}$ at 7 % RH to $\sim 6 \times 10^{-4}$ at 59 % RH, showing a positive dependence on RH. Therefore, it can be concluded that, under similar conditions for the RH range covered in this work, TiO_2 shows higher heterogeneous reactivity than SiO_2 towards $ClONO_2$. Compared to sulfuric acid particles in the lower stratosphere, the heterogeneous reactivity towards $ClONO_2$ is lower for TiO_2 particles. In addition, the heterogeneous uptake of $ClONO_2$ by Pyrex glass was also studied, with $\gamma(ClONO_2)$ increasing from $\sim 4.5 \times 10^{-6}$ at 0 % RH to $\sim 1.6 \times 10^{-5}$ at 24 % RH.

Using the UKCA chemistry–climate model with nudged meteorology, we have constructed a scenario to assess the impact of TiO_2 particle injection on stratospheric chemistry. In this scenario TiO_2 aerosol particles are distributed in the stratosphere in such a way that TiO_2 particle injection is expected to produce a radiative effect similar to that of the Mt Pinatubo eruption, following Pope et al. (2012). Heterogeneous reactions of N_2O_5 and $ClONO_2$ with TiO_2 aerosol particles, both with an uptake coefficient of 1.5×10^{-3} based on our previous (Tang et al., 2014c) and current laboratory experiments, were included in the simulation. It is found that, compared to the eruption of Mt Pinatubo, the TiO_2 injection has a much smaller impact on N_2O_5 in the stratosphere, although significant reduction (20–60 % compared to the background scenario without additional particle injection) in stratospheric N_2O_5 also occurs. Compared to the background scenario, both TiO_2 injection and the Mt Pinatubo eruption scenarios lead to increased stratospheric ClO_x mixing ratios, and the ClO_x mixing ratios are lower for the TiO_2 injection than the Mt Pinatubo eruption. Both TiO_2 injection and the Mt Pinatubo eruption result in significant ozone depletion in the lower stratosphere, with the largest decreases occurring at high latitudes. In comparison with Mt Pinatubo eruption, TiO_2 injection causes less ClO_x activation and less ozone destruction in the lowermost stratosphere, while the reduced depletion of N_2O_5 and NO_x in the middle stratosphere results in decreased ozone levels. Overall, our simulation results suggest that there is no significant difference (within ±2.5 %) in the vertically integrated ozone abundances between TiO_2 injection and Mt Pinatubo eruption.

It should be emphasised that heterogeneous chemistry of TiO_2 included in our current modelling study is not complete. One example is the heterogeneous reaction of $ClONO_2$ with HCl (Reaction R1c) on/in the particles. An uptake coefficient of 0.02 was reported for the heterogeneous reaction of $ClONO_2$ with HCl on Al_2O_3 particles (Molina et al., 1997), and it is reasonable to assume that this reaction may also be quite fast on TiO_2 particles. The heterogeneous reaction of $ClONO_2$ with HCl on TiO_2 particles, with an uptake coefficient assumed to be the same as that on the Al_2O_3 surface (i.e. 0.02) as reported by Molina et al. (1997), has been included in further simulations, and the results will be reported and discussed in a following paper. Other reactions, including the heterogeneous reaction of HOCl (Molina et al., 1996; Solomon, 1999) and a range of heterogeneous photochemical reactions (Chen et al., 2012; George et al., 2015), may also be important and thus deserve further laboratory and modelling investigation. In this work we have only considered heterogeneous chemistry of fresh TiO_2 particles. If injected into the stratosphere, TiO_2 particles would be coated with H_2SO_4, NAT, water ice etc., and heterogeneous reactivity of coated TiO_2 particles could be very different from fresh particles. This important issue should be addressed by further laboratory and modelling studies.

Our nudged modelling simulations, designed to focus on chemistry effects, do not take into account feedbacks between radiative effects, atmospheric dynamics and chemistry. Several recent studies have assessed the impact of high-latitude stratospheric ozone depletion using the UKCA model (Braesicke et al., 2013; Keeble et al., 2014) and have shown that interactive feedbacks can affect stratospheric temperatures, the strength of the Brewer–Dobson circulation, the longevity of polar vortices and surface climate. By nudging the model to observed meteorology during the Mt Pinatubo eruption, these feedbacks are implicitly included in the sulfate injection scenario. However, while we have chosen a TiO_2 loading to give the same surface radiative response as the Mt Pinatubo eruption, the stratospheric radiative impacts may differ. In order to fully understand the true impact of stratospheric particle injection, both the radiative and chemical effects, and the coupling between these responses, need to be explored further. In addition, before any climate engineering schemes could be considered, much consideration is absolutely obligatory, including, but not limited to, technical, socioeconomic, political, environmental and ethical feasibilities.

7 Data availability

The data used in this study are available from M. Tang (mingjintang@gig.ac.cn) and J. Keeble (jmk64@cam.ac.uk) upon request.

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