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Impact of new laboratory studies of N$_2$O$_5$ hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH

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[1] We investigate the impact of new laboratory studies of N$_2$O$_5$ hydrolysis in aerosols on global model simulations of tropospheric chemistry. We use data from these new studies to parameterize the reaction probability ($\gamma_{N2O5}$) in the GEOS-CHEM global model as a function of local aerosol composition, temperature, and relative humidity. We find a much lower global mean $\gamma_{N2O5}$ (0.02) than commonly assumed in models (0.1). Relative to a model simulation assuming a uniform $\gamma_{N2O5} = 0.1$, we find increases in mass-averaged tropospheric NO$_x$, O$_3$, and OH concentrations of 7%, 4%, and 8% respectively. The increases in NO$_x$ and O$_3$ concentrations bring the GEOS-CHEM simulation in better agreement with climatological observations.


1. Introduction

[2] Reactive oxides of nitrogen (NO$_x$ ≡ NO + NO$_2$) play a defining role in the chemistry of the troposphere. They react catalytically to produce ozone (O$_3$) and OH, the main tropospheric oxidants. The dominant global source of NO$_x$ is the burning of fossil fuel (20–33 Tg N yr$^{-1}$) with minor contributions from biomass and biofuel burning (collectively 3–13 Tg N yr$^{-1}$), soils (4–7 Tg N yr$^{-1}$), and lightning (3–13 Tg N yr$^{-1}$) [Intergovernmental Panel on Climate Change (IPCC), 2001]. NO$_x$ is permanently removed from the atmosphere by conversion to nitric acid followed by deposition. During the day, this conversion occurs through the reaction of NO$_x$ with OH, and during the night by hydrolysis of N$_2$O$_5$ in aerosols. These mechanisms are globally comparable as sinks of NO$_x$ [Dentener and Crutzen, 1993]. Previous evaluations of the literature based upon work undertaken for stratospheric conditions [Jacob, 2000] gave a best estimate of 0.1 for the reaction probability of N$_2$O$_5$ (Bart et al., 2001; Tie et al., 2001; Stroud et al., 2003). A study by Tie et al. [2003] found that $\gamma_{N2O5} = 0.04$ or less gave a better simulation of NO$_x$ concentrations observed during the TOPSE aircraft campaign over the North American Arctic. Photochemical model analyses of observed NO$_x$/HNO$_3$ ratios in the upper troposphere have also suggested that $\gamma_{N2O5}$ is much less than 0.1 [McKeen et al., 1997; Schultz et al., 2000]. Recent laboratory studies of N$_2$O$_5$ hydrolysis [Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003] provide sufficient information to improve the representation of $\gamma_{N2O5}$ in global models as a function of local aerosol composition, relative humidity (R.H.), and temperature. We examine here the implications for model simulations of the global tropospheric budgets of NO$_x$, O$_3$, and OH.

2. Model Calculation of N$_2$O$_5$ Reaction Probability

[3] Our analysis uses the GEOS-CHEM chemical transport model (CTM) which has been used previously for a number of studies focused on tropospheric O$_3$-OH-NO$_x$ budgets [e.g., Bey et al., 2001; Martin et al., 2003a; Hudman et al., 2004]. We use GEOS-CHEM version 5-07-08 (http://www-as.harvard.edu/chemistry/trop/geos). This version of the model considers five different aerosol components: dust, sulfate, organic carbon, black carbon, and sea salt. The sulfate aerosol mass concentration is calculated within the model [Park et al., 2004] and the mass concentration of the other components are specified as 3-D monthly mean values from the GOCART model [Chin et al., 2000a, 2000b; Ginoux et al., 2001; Martin et al., 2003b]. Size distributions for all aerosol components are specified as described by [Martin et al., 2003b].

[4] Past applications of GEOS-CHEM have assumed $\gamma_{N2O5} = 0.1$ for all aerosol types and conditions. In the present study we specify $\gamma_{N2O5}$ for different aerosol components and conditions on the basis of recent laboratory studies [Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003]. Kane et al. [2001] investigated the effect of R.H. over the range 8–92% on $\gamma_{N2O5}$ for ammonium sulfate, ammonium bisulfate, and sulfuric acid aerosols. We assume here that atmospheric sulfate aerosol is mainly present as ammonium sulfate, a reasonable assumption at least over continental regions [Martin et al., 2004] where N$_2$O$_5$ hydrolysis is globally most important. Kane et al. [2001] found that $\gamma_{N2O5}$ increases smoothly from 9.4 × 10$^{-12}$ at 8% R.H. to $0.042$ at 92%. Hallquist et al. [2003] investigated the effect of temperature and found that $\gamma_{N2O5}$ for ammonium sulfate had a roughly constant value of 0.03 up to 280 K with a rapid decrease to 0.003 at 308 K. For our study we have adopted the R.H. parameterization of Kane et al. [2001] and the temperature dependence of Hallquist et al. [2003]. Thornton et al. [2003] investigated N$_2$O$_5$ uptake by organic aerosols using malonic acid particles. They found $\gamma_{N2O5}$ on solid aerosol (R.H. between 0 and 50%) to be 0.001. For aqueous aerosols, $\gamma_{N2O5}$ increased from
0.01 to 0.03 as R.H. increased from 20 to 50%, (between 20 and 50% R.H. a metastable state exists) with values remaining constant at around 0.03 for R.H. above this. It appears that for much of the atmosphere organic aerosols are aqueous [Bradan and Abbatt, 2004; Marcolli et al., 2004] so we assume here the aqueous range of values.

Table 1 describes the updated parameterization of $\gamma_{N_2O_5}$ in GEOS-CHEM based on these and other data. We present here results from two one-year GEOS-CHEM simulations for 2001. The first simulation uses a uniform $\gamma_{N_2O_5} = 0.1$ and the second uses the parameterization described in Table 1. Both simulations were initialized with a 12-month spin-up. The horizontal resolution used is 4° × 5° and there are 30 vertical layers from the surface to 50 hPa. Further details of the tropospheric chemistry simulations in GEOS-CHEM are presented, for example, by Bey et al. [2001] and Martin et al. [2003a].

Figure 1 shows the zonal mean $\gamma_{N_2O_5}$ values for January and July as computed in GEOS-CHEM from the data in Table 1. $\gamma_{N_2O_5}$ for each grid-box is calculated as the mean $\gamma_{N_2O_5}$ over all aerosol components weighted by the relative contribution of each component to the total aerosol surface area of that grid-box. Much of the spatial and seasonal variability in Figure 1 reflects the temperature and R.H. dependences of $\gamma_{N_2O_5}$ on sulfate aerosol. Values are highest in surface air at the summertime poles and at northern mid-latitudes in winter because of cold temperatures, high R.H., and a large contribution of sulfate to the total aerosol surface area. The general decrease of $\gamma_{N_2O_5}$ with altitude is due to the decrease in R.H., leading to minima in the very low R.H. downward branches of the Hadley circulation. The global mean $\gamma_{N_2O_5}$ is 0.02. During the spring months in the Arctic, $\gamma_{N_2O_5}$ ranges from 0.01 to 0.04 which is within the range found by Tie et al. [2003] to match the TOPSE NOx observations. The low values in the upper troposphere (~0.01) are consistent with HNO3/NOx concentration ratios measured from aircraft [McKeen et al., 1997; Schulz et al., 2000].

3. Impact on Global Model Budgets

Figure 2 shows the calculated zonal mean fractional change in the concentrations of NOx, O3 and OH for Dec–Feb and Jun–Aug with the new parameterization for $\gamma_{N_2O_5}$.
as compared to the simulation with $\gamma_{N2O5} = 0.1$. The tropospheric NO$_x$ burden increases from 9.6 Gg N to 10.2 Gg N (7%). The largest increases (~50%) are found in winter in the downwind branch of the Hadley circulation, consistent with the reduction in $\gamma_{N2O5}$ associated with these dry warm conditions (Figure 1). On a global mass-weighted basis, N$_2$O$_5$ concentrations are 250% higher and NO$_3$ concentrations are 30% higher. Comparison of model results with a compilation of aircraft observations of NO$_3$ concentrations mapped onto a monthly $4^\circ \times 5^\circ$ grid [Emmons et al., 2000] shows a reduction in the mass-weighted model bias from -14.0 pptv to -7.9 pptv with the new $\gamma_{N2O5}$ parameterization. The mean ratio of simulated to observed NO$_3$ concentrations for that compilation increases from 0.77 to 0.86. The largest change is in the middle troposphere (3–10km) where the mean ratio increases from 0.79 to 0.91.

[8] Simulated O$_3$ concentrations increase with the new N$_2$O$_5$ hydrolysis parameterization, responding to the increased NO$_x$ concentrations. The total burden of tropospheric O$_3$ increases by 4% from 249 Gg to 260 Gg. Comparison with the climatological compilation of tropospheric ozone data by [Logan, 1999] shows a reduction in the mass-weighted model bias from -2.9 ppbv to -1.4 ppbv. The mass-weighted model to measured concentration ratio improves from 0.94 to 0.99. The global O$_3$ (odd oxygen) chemical production increases within the troposphere by 7% from 3900 Tg O$_3$ yr$^{-1}$ to 4180 Tg O$_3$ yr$^{-1}$. An intercomparison between 10 global tropospheric chemistry models [IPCC, 2001] found a global mean O$_3$ production rate of 3365 ± 745 Tg O$_3$ yr$^{-1}$ across all the models. GEOS-CHEM is at the high end of this range, but we have argued that this could reflect biases in other models [Bey et al., 2001].

[9] The combined effect of increasing the NO$_x$ and O$_3$ mass is an increase in the concentration of OH. The mass-weighted, global annual mean tropospheric OH concentration increases from 0.99 $\times$ 10$^6$ cm$^{-3}$ to 1.08 $\times$ 10$^6$ cm$^{-3}$ (an 8% increase). Both values are consistent with the current constraints on global mean OH concentrations based on methyl-chloroform observations: 1.07 ($\pm$0.09 $\pm$0.17) $\times$ 10$^6$ cm$^{-3}$ [Krol et al., 1998], 1.16 ± 0.17 $\times$ 10$^6$ cm$^{-3}$ [Spivakovsky et al., 2000], and 0.94 ± 0.13 $\times$ 10$^6$ cm$^{-3}$ [Prinn et al., 2001].

[10] The new parameterization for $\gamma_{N2O5}$ described in Table 1 thus has significant impact on simulations of tropospheric composition and points to the need for further work to characterize N$_2$O$_5$ uptake by aerosols. There are to our knowledge no laboratory data for $\gamma_{N2O5}$ on dust aerosols, which make a large contribution to total aerosol surface area. Uncertainties in organic aerosol phase, and in the mixing states between different aerosol types, are also major issues.

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References


