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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 (γ$_{N2O5}$) in the GEOS-CHEM global model as a function of local aerosol composition, temperature, and relative humidity. We find a much lower global mean γ$_{N2O5}$ (0.02) than commonly assumed in models (0.1). Relative to a model simulation assuming a uniform γ$_{N2O5}$ = 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. Citation: Evans, M. J., and D. J. Jacob (2005), Impact of new laboratory studies of N$_2$O$_5$ hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophys. Res. Lett., 32, L09813, doi:10.1029/2005GL022469.

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$_5$ (γ$_{N2O5}$), i.e. the probability that a N$_2$O$_5$ molecule impacting an aerosol surface undergoes reaction. This value has been the standard used in many tropospheric chemistry models [Dentener and Crutzen, 1993; Wang et al., 1998; Bey et al., 2001; Tie et al., 2001; Stroud et al., 2003]. A study by Tie et al. [2003] found that γ$_{N2O5}$ = 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 γ$_{N2O5}$ 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 γ$_{N2O5}$ 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 γ$_{N2O5}$ = 0.1 for all aerosol types and conditions. In the present study we specify γ$_{N2O5}$ 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 γ$_{N2O5}$ 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 γ$_{N2O5}$ increases smoothly from 9.4 × 10$^{-9}$ at 8% R.H. to 0.042 at 92%. Hallquist et al. [2003] investigated the effect of temperature and found that γ$_{N2O5}$ 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 γ$_{N2O5}$ on solid aerosol (R.H. between 0 and 50%) to be 0.001. For aqueous aerosols, γ$_{N2O5}$ increased from...
Table 1. GEOS-CHEM Representation of the Reaction Probability \(\gamma_{N2O5}\) for \(N2O5\) Hydrolysis on Aerosol Surfaces

<table>
<thead>
<tr>
<th>Aerosol Type</th>
<th>Reaction Probability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate(^b)</td>
<td>(\gamma = \alpha \times 10^\beta)</td>
<td>Kane et al. [2001]</td>
</tr>
<tr>
<td></td>
<td>(\alpha = 2.79 \times 10^{-4} + 1.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\times 10^{-4} \times RH + 3.43)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\times 10^{-4} \times RH^2 + 7.52)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\times 10^{-4} \times RH^3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\beta = 4 \times 10^{-2})</td>
<td>Hallquist et al. [2003](^c)</td>
</tr>
<tr>
<td></td>
<td>(\times (T-294)) ((T &gt; 282K))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\beta = -0.48) ((T &lt; 282K))</td>
<td></td>
</tr>
<tr>
<td>Organic carbon</td>
<td>(\gamma = RH \times 5.2)</td>
<td>Thornton et al. [2003](^d)</td>
</tr>
<tr>
<td></td>
<td>(\times 10^{-4}) ((RH &lt; 57%))</td>
<td></td>
</tr>
<tr>
<td>Black carbon</td>
<td>(\gamma = 0.005)</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>Sea salt</td>
<td>(\gamma = 0.005) ((RH &lt; 62%))</td>
<td>Sander et al. [2003](^e)</td>
</tr>
<tr>
<td></td>
<td>(\gamma = 0.03) ((RH &gt; 57%))</td>
<td></td>
</tr>
<tr>
<td>Dust</td>
<td>(\gamma = 0.03)</td>
<td>Bauer et al. [2004](^f)</td>
</tr>
</tbody>
</table>

\(^a\)T is temperature (K), RH is relative humidity (%).  
\(^b\)We assume a separable relationship between R.H. and temperature effects on \(\gamma_{N2O5}\), using the work by Kane et al. [2001] for the R.H. effect and Hallquist et al. [2003] for the temperature effect.  
\(^c\)Logarithmic fit of data presented in Figure 11 of Hallquist et al. [2003].  
\(^d\)Linear fit of data presented in Figure 6 of Thornton et al. [2003].  
\(^e\)We use the work of Sander et al. [2003] for the reaction probability on dry and aqueous sea-salt aerosol, and assume that the aerosol is dry for RH < 62%, corresponding to the midpoint between deliquescence and efflorescence R.H. [Martin, 2000].  
\(^f\)No value available from published literature. Bauer et al. [2004] quote a range from 0.003 to 0.02 from unpublished measurements by J. Crowley as part of the MINATROC EU Commission project EVK2-CT-1999-00003.

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 \(\gamma_{N2O5}\) 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 \(\gamma_{N2O5} = 0.1\) 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 \(4^\circ \times 5^\circ\) 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 \(\gamma_{N2O5}\) values for January and July as computed in GEOS-CHEM from the data in Table 1. \(\gamma_{N2O5}\) for each grid-box is calculated as the mean \(\gamma_{N2O5}\) 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 \(\gamma_{N2O5}\) 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 \(\gamma_{N2O5}\) 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 \(\gamma_{N2O5}\) is 0.02. During the spring months in the Arctic, \(\gamma_{N2O5}\) ranges from 0.01 to 0.04 which is within the range found by Tie et al. [2003] to match the TOPSE NO\(_x\) observations. The low values in the upper troposphere (~0.01) are consistent with HNO\(_3\)/NO\(_x\) concentration ratios measured from aircraft [McKeen et al., 1997; Schultz et al., 2000].

3. Impact on Global Model Budgets

Figure 2 shows the calculated zonal mean fractional change in the concentrations of NO\(_x\), O\(_3\), and OH for Dec–Feb and Jun–Aug with the new parameterization for \(\gamma_{N2O5}\).
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 downward 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° × 5° 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.

Simulation O$_3$ concentrations increase with the new N$_2$O$_5$ hydrolysis parameterization, responding to the increased NO$_2$ 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].

The combined effect of increasing the NO$_x$ and O$_3$ concentrations is an increase in the concentration of OH. The mass-weighted, global annual mean tropospheric OH concentration increases from 0.99 × 10$^6$ cm$^{-3}$ to 1.08 × 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 (±0.09, ±0.17) × 10$^6$ cm$^{-3}$ [Krol et al., 1998], 1.16 ± 0.17 × 10$^6$ cm$^{-3}$ [Spivakovsky et al., 2000], and 0.94 ± 0.13 × 10$^6$ cm$^{-3}$ [Prinn et al., 2001].

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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