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Impact of new laboratory studies of N₂O₅ 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 N₂O₅ hydrolysis in aerosols on global model simulations of tropospheric chemistry. We use data from these new studies to parameterize the reaction probability ($\gamma_{\text{N}_2\text{O}_5}$) in the GEOS-CHEM global model as a function of local aerosol composition, temperature, and relative humidity. We find a much lower global mean $\gamma_{\text{N}_2\text{O}_5}$ (0.02) than commonly assumed in models (0.1). Relative to a model simulation assuming a uniform $\gamma_{\text{N}_2\text{O}_5} = 0.1$, we find increases in mass-averaged tropospheric NO_x, O₃, and OH concentrations of 7%, 4%, and 8% respectively. The increases in NO_x and O₃ concentrations bring the GEOS-CHEM simulation in better agreement with climatological observations.

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1. Introduction

[2] Reactive oxides of nitrogen (NO_x ≡ NO + NO₂) play a defining role in the chemistry of the troposphere. They react catalytically to produce ozone (O₃) 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 NO₂ with OH, and during the night by hydrolysis of N₂O₅ 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 N₂O₅ ($\gamma_{\text{N}_2\text{O}_5}$), i.e. the probability that a N₂O₅ 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 $\gamma_{\text{N}_2\text{O}_5} = 0.04$ 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/HNO₃

ratios in the upper troposphere have also suggested that $\gamma_{\text{N}_2\text{O}_5}$ is much less than 0.1 [McKeen et al., 1997; Schultz et al., 2000]. Recent laboratory studies of N₂O₅ hydrolysis [Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003] provide sufficient information to improve the representation of $\gamma_{\text{N}_2\text{O}_5}$ 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, O₃, and OH.

2. Model Calculation of N₂O₅ 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 O₃-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 $\gamma_{\text{N}_2\text{O}_5} = 0.1$ for all aerosol types and conditions. In the present study we specify $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$ 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 N₂O₅ hydrolysis is globally most important. Kane et al. [2001] found that $\gamma_{\text{N}_2\text{O}_5}$ increases smoothly from 9.4×10^{-4} at 8% R.H. to 0.042 at 92%. Hallquist et al. [2003] investigated the effect of temperature and found that $\gamma_{\text{N}_2\text{O}_5}$ 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 N₂O₅ uptake by organic aerosols using malonic acid particles. They found $\gamma_{\text{N}_2\text{O}_5}$ on solid aerosol (R.H. between 0 and 50%) to be 0.001. For aqueous aerosols, $\gamma_{\text{N}_2\text{O}_5}$ increased from

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Table 1. GEOS-CHEM Representation of the Reaction Probability $\gamma_{\text{N}_2\text{O}_5}$ for N₂O₅ Hydrolysis on Aerosol Surfaces

Aerosol Type	Reaction Probability ^a	Reference
Sulfate ^b	$\gamma = \alpha \times 10^{\beta}$ $\alpha = 2.79 \times 10^{-4} + 1.3$ $\times 10^{-4} \times \text{RH} - 3.43$ $\times 10^{-6} \times \text{RH}^2 + 7.52$ $\times 10^{-8} \times \text{RH}^3$ $\beta = 4 \times 10^{-2}$ $\times (\text{T}-294)$ ($\text{T} \geq 282\text{K}$) $\beta = -0.48$ ($\text{T} < 282\text{K}$)	<i>Kane et al.</i> [2001] <i>Hallquist et al.</i> [2003] ^c
Organic carbon	$\gamma = \text{RH} \times 5.2$ $\times 10^{-4}$ ($\text{RH} < 57\%$) $\gamma = 0.03$ ($\text{RH} \geq 57\%$)	<i>Thornton et al.</i> [2003] ^d
Black carbon	$\gamma = 0.005$	<i>Sander et al.</i> [2003]
Sea salt	$\gamma = 0.005$ ($\text{RH} < 62\%$) $\gamma = 0.03$ ($\text{RH} \geq 62\%$)	<i>Sander et al.</i> [2003] ^e
Dust	$\gamma = 0.01$	<i>Bauer et al.</i> [2004] ^f

^aT is temperature (K), RH is relative humidity (%).

^bWe assume a separable relationship between R.H. and temperature effects on $\gamma_{\text{N}_2\text{O}_5}$, using the work by *Kane et al.* [2001] for the R.H. effect and *Hallquist et al.* [2003] for the temperature effect.

^cLogarithmic fit of data presented in Figure 11 of *Hallquist et al.* [2003].

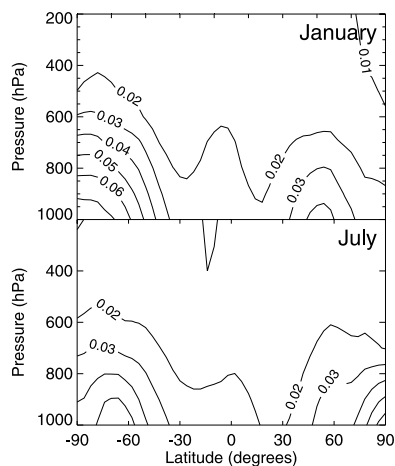
^dLinear fit of data presented in Figure 6 of *Thornton et al.* [2003].

^eWe 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 $\text{RH} < 62\%$, corresponding to the midpoint between deliquescence and efflorescence R.H. [*Martin*, 2000].

^fNo 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; *Marcilli et al.*, 2004] so we assume here the aqueous range of values.

[5] Table 1 describes the updated parameterization of $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5} = 0.1$ 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 $4^\circ \times 5^\circ$ and there are 30 vertical layers from the surface

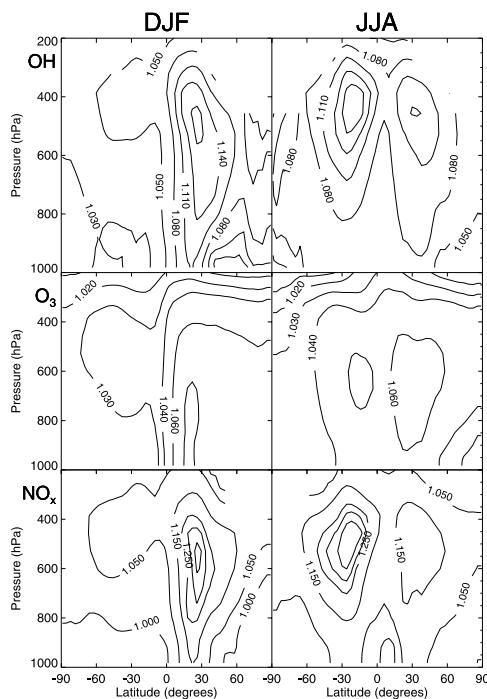
**Figure 1.** Zonal mean N₂O₅ reaction probabilities ($\gamma_{\text{N}_2\text{O}_5}$) for January and July 2001, calculated in the GEOS-CHEM global model using the expressions of Table 1.

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].

[6] Figure 1 shows the zonal mean $\gamma_{\text{N}_2\text{O}_5}$ values for January and July as computed in GEOS-CHEM from the data in Table 1. $\gamma_{\text{N}_2\text{O}_5}$ for each grid-box is calculated as the mean $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$ is 0.02. During the spring months in the Arctic, $\gamma_{\text{N}_2\text{O}_5}$ 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 HNO₃/NO_x concentration ratios measured from aircraft [*McKeen et al.*, 1997; *Schultz et al.*, 2000].

3. Impact on Global Model Budgets

[7] Figure 2 shows the calculated zonal mean fractional change in the concentrations of NO_x, O₃ and OH for Dec–Feb and Jun–Aug with the new parameterization for $\gamma_{\text{N}_2\text{O}_5}$,

**Figure 2.** Calculated zonal mean concentration ratios of OH, ozone, and NO_x for GEOS-CHEM model simulations with $\gamma_{\text{N}_2\text{O}_5}$ values calculated from Table 1 versus a uniform value of 0.1. Results are seasonal averages for winter (DJF) and summer (JJA). Values greater than 1 indicate higher concentrations with the $\gamma_{\text{N}_2\text{O}_5}$ values calculated from Table 1 than with a uniform $\gamma_{\text{N}_2\text{O}_5}$ of 0.1.

as compared to the simulation with $\gamma_{\text{N}_2\text{O}_5} = 0.1$. 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 $\gamma_{\text{N}_2\text{O}_5}$ associated with these dry warm conditions (Figure 1). On a global mass-weighted basis, N₂O₅ concentrations are 250% higher and NO₃ concentrations are 30% higher. Comparison of model results with a compilation of aircraft observations of NO_x 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 $\gamma_{\text{N}_2\text{O}_5}$ parameterization. The mean ratio of simulated to observed NO_x 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 O₃ concentrations increase with the new N₂O₅ hydrolysis parameterization, responding to the increased NO_x concentrations. The total burden of tropospheric O₃ increases by 4% from 249 Gg to 260 Gg. Comparison with the climatological compilation of tropospheric ozonesonde 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_x (odd oxygen) chemical production increases within the troposphere by 7% from 3900 Tg O₃ yr⁻¹ to 4180 Tg O₃ yr⁻¹. An intercomparison between 10 global tropospheric chemistry models [IPCC, 2001] found a global mean O_x production rate of 3365 ± 745 Tg O₃ 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 O₃ concentrations is an increase in the concentration of OH. The mass-weighted, global annual mean tropospheric OH concentration increases from 0.99 × 10⁶ cm⁻³ to 1.08 × 10⁶ 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) × 10⁶ cm⁻³ [Krol *et al.*, 1998], 1.16 ± 0.17 × 10⁶ cm⁻³ [Spivakovsky *et al.*, 2000], and 0.94 ± 0.13 × 10⁶ cm⁻³ [Prinn *et al.*, 2001].

[10] The new parameterization for $\gamma_{\text{N}_2\text{O}_5}$ described in Table 1 thus has significant impact on simulations of tropospheric composition and points to the need for further work to characterize N₂O₅ uptake by aerosols. There are to our knowledge no laboratory data for $\gamma_{\text{N}_2\text{O}_5}$ 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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