PARAMETERIZATION OF N_2O_5 REACTION PROBABILITIES FOR INCLUSION IN CMAQ

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1. INTRODUCTION

Heterogeneous reactions of N_2O_5 have a substantial influence on gaseous and particulate pollutant concentrations. To accurately simulate nighttime nitrogen chemistry and the resulting impacts on ozone, particulate nitrate, and nitrogen oxides, air quality models must contain a reliable parameterization of the heterogeneous reaction probability, γ, which is defined as the fraction of collisions between gaseous N_2O_5 molecules and particle surfaces that lead to the production of HNO_3.

Bhave et al. (2006) updated the parameterization of γ in the Community Multiscale Air Quality (CMAQ) model v4.6 based on an equation by Evans and Jacob (2005), referred to hereafter as EJ05. Later, we discovered a typographical error in that equation. The form of their equation should read $\gamma = \alpha \times 10^{-\beta}$ but the negative sign was accidentally omitted from the publication (Mathew Evans, personal communication). Correction of that typographical error led to a substantial degradation in wintertime model performance for particulate NO_3^-. In the process of diagnosing this problem, we found a few other shortcomings in EJ05 so we began an effort to derive a new parameterization of γ. Results of our efforts are described on this poster.

Our work has several advantages over previous studies: (1) our parameterization uses all published laboratory measurements of γ on ammoniated sulfate and nitrate particles; (2) rigorous statistical methods are employed (e.g., significance test of each independent variable, weighting of each data point by the measurement uncertainty, defining extrapolation limits) leading to a simple formula that captures the most important features in the laboratory data; (3) the effect of particulate nitrate to suppress γ is quantified using measurements that are representative of continental, rather than marine, conditions; (4) the effect of particle acidity to enhance γ is accounted for; and (5) phase changes are considered explicitly in our parameterization such that γ on aqueous particles exceeds that on solid particles.

2. LABORATORY DATA

All the data used for our examination of γ with respect to T, RH, and particle composition come from laboratory work documented in the following publications: Mozurkewich and Calvert (1988); Hu and Abbatt (1997); Folkers (2001); Kane et al. (2001); Folkers et al. (2003); Hallquist et al. (2003); Badger et al. (2006). For brevity, these documents will be referred to hereafter as MOZ88, HU97, FOL01, KAN01, FOL03, HAL03, and BAD06, respectively. To our knowledge, these seven publications contain all of the published laboratory measurements of γ on ammoniated sulfate and nitrate particles at conditions relevant to the troposphere. We focus on these particle compositions because they constitute a substantial portion of the aerosol surface area in continental air masses and because laboratory measurements of γ on these surfaces are relatively abundant.

Figure 2 on the poster summarizes all 78 of the laboratory measurements used to develop our statistical parameterization, and illustrates the dependence of γ on RH, T, particle composition, and phase state. For all four particle types studied here, the most prominent feature, with a few exceptions, is that γ increases with RH. For a fixed RH and T, γ is highest on aqueous NH_4HSO_4 (see Fig. 2a), relatively high on aqueous $(NH_4)_2SO_4$ (Fig. 2b), quite low on aqueous NH_4NO_3 (Fig. 2c), and lowest on the dry ammoniated sulfate particles (Fig. 2d). A successful statistical model must capture these features of the laboratory data.

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3. METHODS

3.1 Statistical Models for Aqueous Particles

Prior to our regression analyses, the laboratory data were transformed using the logit function: $\lambda = \ln\left(\gamma/(1-\gamma)\right)$. This transformation ensures that all model estimates of γ lie between zero and one, which is consistent with the relative-frequency definition of γ. One regression equation was estimated from the union of aqueous NH_4HSO_4 and $(NH_4)_2SO_4$ data for which observations are most abundant. A second regression equation based on the NH_4NO_3 data was fit separately since those measurements were reported in a separate study (FOL01) from all the ammoniated sulfate data and include only four unique combinations of T and RH values.

On aqueous NH_4HSO_4 and $(NH_4)_2SO_4$ particles, a dependence of γ on temperature is difficult to observe in the measurements. The only cross sections of data where temperature was varied over a large range are at 50% RH (see Fig. 2a and 2b). Along those cross sections, the γ values do not change monotonically with temperature. Based on HAL03, EJ05, and our own data analyses, a temperature threshold, j, was applied within our statistical model. The threshold temperature variable is defined as:

$$T_j = \begin{cases} T - j & T > j \\ 0 & T \le j \end{cases}$$

Our initial form of the statistical model for aqueous NH_4HSO_4 and $(NH_4)_2SO_4$ particles, denoted λ_1 and λ_2, respectively, is given by:

$$\lambda_1 = \beta_{10} + \beta_{11}RH + \beta_{12}T_j + \beta_{13}RH \times T_j$$
$$+ \beta_{14}RH^2 + \beta_{15}RH^3 + \varepsilon_1 \tag{1}$$

$$\lambda_2 = (\beta_{10} + \beta_{20}) + (\beta_{11} + \beta_{21})RH$$
$$+ (\beta_{12} + \beta_{22})T_j + (\beta_{13} + \beta_{23})RH \times T_j$$
$$+ (\beta_{14} + \beta_{24})RH^2 + (\beta_{15} + \beta_{25})RH^3 \tag{2}$$
$$+ \varepsilon_2$$

The model errors were assumed to be normally and independently distributed. Higher order polynomial terms were considered for *RH*, but not T_j, based on our inspection of plots of λ versus RH and T. Note that during the regression analysis, Eqs. (1) and (2) were solved simultaneously using the combination of aqueous NH_4HSO_4 and

$(NH_4)_2SO_4$ data. The extra coefficients – β_{20}, β_{21}, β_{22}, β_{23}, β_{24}, and β_{25} – in Eq. (2) were included to test whether the linear relationship between λ, *RH*, and T_j, differs significantly for different particle compositions.

Coefficients of the linear model were estimated using weighted least squares (Kutner et al. 2005). Each observation was assigned a weight, *w*, that is a function of the standard error values, σ, reported with each laboratory measurement of γ:

$$w = \left[\gamma(1-\gamma)\right]^2 / \sigma^2 \tag{3}$$

These weights were derived based on a Taylor approximation for the estimate of the variance of λ (Casella and Berger, 2002, pg 241).

Stepwise model selection for regression analysis was used to determine which of the variables in Eqs. (1) and (2) are statistically significant. At each stage of the model selection process, the Akaike Information Criterion (AIC) was used to decide whether linear terms, cross product terms, and higher order terms should be included or excluded. This process was repeated for each integer value of *j* between 275 K and 295 K as well as for a model with no temperature threshold (i.e. *j* = 0 K). The AIC value was used to determine the most parsimonious statistical model that best fits the data with a minimum number of covariates (Akaike, 1973). This procedure yielded a model with four statistically significant terms and a threshold temperature of *j* = 287 K. The individual equations for aqueous NH_4HSO_4 and $(NH_4)_2SO_4$ differ only in the intercept term.

$$\lambda_1 = \beta_{10} + \beta_{11}RH + \beta_{12}T_{287} \tag{4}$$
$$\lambda_2 = (\beta_{10} + \beta_{20}) + \beta_{11}RH + \beta_{12}T_{287} \tag{5}$$

The best-fit values and standard errors of each coefficient are given in Table 1 on the poster.

For aqueous NH_4NO_3 particles, all data were collected in a narrow temperature range so it was not possible to identify a temperature trend. The model for NH_4NO_3 was selected to match the form of Eq. (1), and is given by the following equation:

$$\lambda_3 = \beta_{30} + \beta_{31}RH \tag{6}$$

The estimated coefficients for this model are also given in Table 1.

Equations (4– 6) are back transformed to compute the reaction probability values for the three aqueous particle compositions.

$$\gamma_i = \frac{1}{1 + e^{-\lambda_i}} \quad i = 1, 2, 3 \tag{7}$$

In the upper panel of Fig. 3, the parameterized functions for γ are plotted on a log scale versus

RH for a selected set of temperatures. The lower panel of Fig. 3 shows contour plots of the estimated γ values spanning the ranges of T and RH encountered in the lower troposphere. Each laboratory measurement is shown as a discrete point in the lower panel. Laboratory data are not available over the entire range of tropospheric conditions, so caution must be exercised when extrapolating parameterizations derived from the available data. For example, extrapolation of the regression equations to the regime of low T and high RH yields γ values which exceed all of the lab measurements (e.g., $\gamma_1 > 0.15$). To prevent erroneous extrapolations when these functions are used in air quality models, the estimated γ values were constrained to be no greater than the maximum observed γ:

$$\gamma_1^* = \min(\gamma_1, 0.08585)$$

$$\gamma_2^* = \min(\gamma_2, 0.053) \tag{8}$$

$$\gamma_3^* = \min(\gamma_3, 0.0154)$$

These upper limits are depicted by horizontal gray lines in Fig. 3a-c, and the lightly-shaded pentagons in the lower-right portions of Fig. 3d-f.

Extrapolation of Eqs. (4–7) must also be limited by thermodynamic considerations. At RH < 32.8%, $(NH_4)_2SO_4$ crystallizes to form a solid phase (Martin et al., 2003) and γ_2 is not expected to decline smoothly with decreasing RH across this phase boundary. The regions of Fig. 2b and 2e with RH lower than the crystallization relative humidity (CRH) are shaded to illustrate this limit. In contrast, aqueous droplets containing pure NH_4HSO_4 or pure NH_4NO_3 do not crystallize (Martin et al., 2003) so our equations for γ_1 and γ_3 may be applicable at very low RH.

Under the conditions of very high RH and low T encountered occasionally in the lower troposphere, particle-bound water will freeze to form ice. The point at which this phase change occurs is determined by the ratio of the saturation vapor pressure over ice (pw_{ice}) to that over water (pw_{water}). This portion of the phase diagram is shaded in the lower panel of Fig. 3, using the Goff-Gratch equations to compute pw_{ice} and pw_{water} (Goff and Gratch, 1946). As RH increases across this phase boundary, we expect γ to differ from the upper limits imposed by Eq. (8).

3.2 Statistical Model for Dry Particles

When the ambient RH is below the deliquescence relative humidity (DRH), ammoniated sulfate and nitrate can exist as dry particles that are devoid of liquid water. For dry particles, a separate parameterization is needed for γ. The statistical methodology outlined in Section 3.1 was repeated using the 15 dry particle data points in Fig. 2d except, this time, higher order polynomial terms of *RH* were not considered due to the very limited sample size. The variable selection procedure yielded a model with three statistically significant terms and a threshold temperature of 293 K. Analogous to Eq. (2), extra coefficients were included to test whether the linear relationship between λ, *RH*, and T_j, differs for different particle compositions, but none of those coefficients were deemed significant. The model for dry particles (denoted with subscript "d" for dry) is given by

$$\lambda_d = \beta_{d0} + \beta_{d1}RH + \beta_{d2}T_{293} \tag{9}$$

The best-fit values and standard errors of each coefficient are given in Table 1. The estimated values of λ_d can be back transformed using Eq. (7). As with the aqueous parameterizations, estimated γ values were constrained to be no greater than the maximum observed γ:

$$\gamma_d^* = \min(\gamma_d, 0.0124) \tag{10}$$

Recall that no laboratory measurements of γ on dry NH_4NO_3 were found, so Eqs. (9–10) are intended primarily for dry ammoniated sulfate particles.

3.3 Model for Internally-Mixed Particles

In the CMAQ model, inorganic fine particles are often assumed to exist as an internal mixture of SO_4^{2-}, NO_3^-, NH_4^+, and H_2O. To date, laboratory measurements of γ on such mixtures have not been reported. As a provisional measure, it is useful to express γ as a molar-weighted average of the single-component parameterizations provided above. Assuming all of the NO_3^- is present as NH_4NO_3 and the leftover NH_4^+ is distributed between $(NH_4)_2SO_4$ and NH_4HSO_4, we computed mole fractions

$$x_1 = 1 - (x_2 + x_3)$$

$$x_2 = \max\left(0, \min\left(1 - x_3, \frac{A}{N + S} - 1\right)\right) \tag{11}$$

$$x_3 = \frac{N}{N + S}$$

where x_i represents the molar concentration of component *i* normalized by the summed concentrations of NH_4HSO_4, $(NH_4)_2SO_4$, and NH_4NO_3; and *A*, *N*, and *S*, represent the molar concentra-

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tions of particle-phase NH_4^+, NO_3^-, and SO_4^{2-}, respectively. The limiting values of x_2 correspond to mixtures that are more acidic than NH_4HSO_4 or more alkaline than $(NH_4)_2SO_4$. Such compositions are rarely found in tropospheric fine particles, but were considered in Eq. (11) for completeness.

Using the above mole fractions as weighting factors, the reaction probability of N_2O_5 on mixed aqueous particles, $\gamma_{aq,mix}$, can be computed as

$$\gamma_{aq,mix} = \sum_{i=1}^{3} x_i \gamma_i^*$$ (12)

where γ_i^* is defined in Eq. (8). The corresponding expression for mixed dry particles is

$$\gamma_{d,mix} = (x_1 + x_2)\gamma_d^* + x_3 \cdot \min(\gamma_d^*, \gamma_3^*)$$ (13)

In the absence of laboratory measurements on dry NH_4NO_3 particles, the min function is used in Eq. (13) to reflect our expectation that γ on dry NH_4NO_3 particles is similar to γ on dry ammoniated sulfate particles, but should not exceed γ on aqueous NH_4NO_3 particles.

No laboratory measurements of γ on particles containing a mixture of ice and ammoniated sulfate or nitrate were found, but γ on pure ice has been studied extensively for stratospheric applications. A representative γ value of 0.02 was selected from those data (IUPAC, 2006). This fixed value was applied to all ice-containing particles in the present study.

$$\gamma_{ice,mix} = 0.02$$ (14)

4. RESULTS

Among the 78 data points reported in seven different laboratory studies, our parameterizations (i.e., Eqs. (4 – 7, 9) reproduce 53% within a factor of 1.25 and 79% within a factor of two. For comparison, we contrasted this performance with the EJ05 parameterization. When compared against all 40 $(NH_4)_2SO_4$ data points (dry and wet), EJ05 underestimates half of them by 15% or more whereas our parameterization exhibits a smaller median relative bias (+5%). The EJ05 parameterization is not intended for NH_4HSO_4 particles and an erroneous application of EJ05 to such acidic particle surfaces would underestimate most of the NH_4HSO_4 data points by nearly a factor of 2. Similarly, EJ05 should not be applied to NH_4NO_3 particles because it was not designed to capture the nitrate effect on γ.

To illustrate the atmospheric relevance of this work, we applied our parameterizations to conditions representative of the eastern United States

using 3-dimensional fields of T, RH, SO_4^{2-}, NO_3^-, and NH_4^+, obtained from a recent CMAQ model simulation with 12 km horizontal grid spacing (Appel et al., 2007). In that model application, transitions in the aerosol phase state were not simulated. To utilize all of the parameterizations developed in this study, we assume here that the modeled particles are wet above their CRH and dry below their CRH. The CRH for an internally mixed particle composed of SO_4^{2-}, NO_3^-, and NH_4^+ was calculated using the equation for complete crystallization by Martin et al. (2003). Although that equation was only validated at 293 K, we applied it at all T because there currently exists very little data to justify a temperature-dependent CRH. To compute γ over the full range of conditions encountered in the atmosphere, $\gamma_{ambient}$, we applied Eqs. (12–14) as follows:

$$\gamma_{ambient} = \begin{cases} \gamma_{d,mix} & RH < CRH \\ \gamma_{ice,mix} & RH > IRH \\ \gamma_{aq,mix} & otherwise \end{cases}$$ (15)

where IRH is the relative humidity of ice formation, which varies with temperature (see description in Section 3.1).

Values of $\gamma_{ambient}$ were computed for each hour of January, February, July, and August 2001, using T, RH, SO_4^{2-}, NO_3^-, and NH_4^+ in each CMAQ grid cell. For comparison, we also computed hourly spatial fields of γ on NH_4HSO_4 (i.e., γ_1^*), $(NH_4)_2SO_4$ (i.e., γ_2^* when RH ≥ 32.8% and γ_d^* otherwise), and NH_4NO_3 (i.e., γ_3^*), each with the IRH constraint imposed, as well as three other parameterizations of γ that have been applied in air quality models in the past. For illustrative purposes, the hourly γ values were averaged over two-month periods representative of the winter (January – February 2001) and summer (July – August 2001). When averaging hourly values, we included only the nighttime hours of 0400 – 0900 GMT because N_2O_5 concentrations are negligible in the daylight so values of γ at those times have no practical importance. Though vertical distributions of γ were computed, we focused our attention on the model layer that is 75 – 150 m above the surface because the CMAQ results indicate that the product of N_2O_5 and aerosol surface area is highest in this layer during both the summer and winter periods. Recall that the N_2O_5 hydrolysis rate is proportional to this product (Riemer et al., 2003).

Figure 4 on our poster shows results of the above calculations for the January – February

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2001 period. Across the eastern U.S., values of $\gamma_{ambient}$ range from 0.02 over the Midwest to 0.05 over Florida (see Fig. 4d). Low values over the Midwest result from high NO_3^- concentrations, typical of this region during winter, combined with below-freezing temperatures and high RH that occasionally exceeds the IRH (see Fig. 5). The high $\gamma_{ambient}$ values over Florida result from low NO_3^- concentrations coupled with relatively warm temperatures. Comparing Fig. 4d with 4e, it can be seen that our $\gamma_{ambient}$ values fall below the fixed value of 0.1 used in the early work by Dentener and Crutzen (1993) which is now recognized as an upper estimate of γ (Evans and Jacob, 2005). Comparing Fig. 4d with 4f, we see that the γ parameterization by Riemer et al. (2003) is consistently lower than $\gamma_{ambient}$. The Riemer parameterization has an upper bound of 0.02, based on measurements of γ on Na_2SO_4 and $NaHSO_4$ particles. Our parameterization is more appropriate for continental air masses because it is derived from measurements on ammoniated particles rather than sodium-containing particles. Moreover, the Riemer parameterization does not depend on T and RH due to insufficient laboratory data available at the time of that study.

The comparison between $\gamma_{ambient}$ and EJ05 is the most intriguing (compare Fig. 4d and 4g) because EJ05 is the current parameterization of choice in many regional- and global-chemistry models such as CMAQv4.6 and GEOS-CHEM. Across the northern half of the domain, EJ05 often exceeds 0.10 whereas $\gamma_{ambient}$ is between 0.02 and 0.06. At lower latitudes, EJ05 exceeds $\gamma_{ambient}$ by 0.01 to 0.02. Recognizing that $\gamma_{ambient}$ is suppressed by the nitrate effect whereas EJ05 is not, a more equitable comparison is between EJ05 and our parameterization of γ on $(NH_4)_2SO_4$ (i.e., Fig. 4g versus 4b). Surprisingly, this comparison also revealed rather large differences. The main reason for differences in the northern latitudes is that our parameterization was bounded by the maximum laboratory value of 0.053 (see Fig. 3b and 3e) whereas EJ05 yields very large values when extrapolated to low T and high RH conditions. In addition, our values of γ in the north and along the Appalachian Mountains are suppressed by ice formation (see lower-left panel of Fig. 5) whereas the effects of that phase transition are not considered in EJ05. In fact, the very highest values of γ (~0.13) are obtained when EJ05 is extrapolated to the regime where ice formation is favored. In the southern half of the domain, EJ05 exceeds γ_2^* by 0.02 to 0.03. These locations are characterized by

average nighttime conditions of 80% RH and 280 K (see Fig. 5), where EJ05 yields a value of 0.08 and our parameterization reaches its upper-limit value of 0.053.

In the summer, $\gamma_{ambient}$ ranges from 0.01 over Texas and Oklahoma to 0.07 over the Appalachian Mountains (see Fig. 6d). The lowest values correspond to the portion of our domain where the nighttime average temperature was highest (302 K), RH was lowest (60%), and the particle compositions were dominated by $(NH_4)_2SO_4$ ($x_2 = 0.9$). Over the Appalachian Mountains, high values of $\gamma_{ambient}$ resulted from the particle compositions being dominated by NH_4HSO_4 ($x_1 = 0.8$) along with T < 290 K and RH > 80% (see Fig. 7). Across the entire domain, $\gamma_{ambient}$ and EJ05 are in very good agreement (compare Fig. 6d and 6g) except along the Appalachian Mountains where $x_1 = 0.8$. Under those acidic conditions, $\gamma_{ambient}$ exceeds EJ05 by nearly 0.02.

5. CONCLUSIONS

We have developed a comprehensive parameterization for the heterogeneous reaction probability of N_2O_5 as a function of RH, T, particle composition, and phase state, for use in advanced air quality models. We used all published measurements of γ on ammoniated sulfate and nitrate particles, which were compiled from seven different laboratory studies. The final equations are relatively simple, non-linear functions of RH and T that were selected in an objective and statistically rigorous manner. Our parameterization reproduced 79% of the laboratory data within a factor of two and 53% within a factor of 1.25. To our knowledge, this is the first parameterization in which phase changes are considered explicitly such that γ on aqueous particles exceeds that on solid particles. It is also the first parameterization to capture the ~50% enhancement of γ on NH_4HSO_4 particle surfaces relative to $(NH_4)_2SO_4$. Another important result comes from our reevaluation of the nitrate effect using laboratory data on ammoniated particles. That effect, which was previously considered to decrease γ by a factor of ten (Riemer et al., 2003), is now believed to be a factor of 1.4 to 4.4.

Our parameterization was applied under winter and summer conditions representative of the eastern United States using 3-dimensional fields of T, RH, SO_4^{2-}, NO_3^-, and NH_4^+ obtained from a recent CMAQ model simulation. The resulting spatial distributions of γ were contrasted with three other parameterizations that have been applied in

air quality models in the past. Our ambient estimates of γ fall between the upper value proposed by Dentener and Crutzen (1993) and the rather low values used by Riemer et al. (2003). Under winter conditions, large differences were found between our parameterization and that of Evans and Jacob (2005). These comparisons helped us identify critical gaps in the laboratory data that will be most valuable for future refinements of the γ parameterization.

Acknowledgements

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