

4.1 The Effect of Heterogeneous Reactions on Model Performance for Nitrous Acid

Golam Sarwar, Robin L. Dennis and Bernhard Vogel

Abstract Recent studies suggest that emissions, heterogeneous reactions, and surface photolysis of adsorbed nitric acid may produce additional nitrous acid in the atmosphere. The effects of these sources on nitrous acid formation are evaluated using the Community Multiscale Air Quality modeling system. Predicted nitrous acid with and without these sources are compared with observed data from northeast Philadelphia. The incorporation of these sources greatly improves the model performance for nitrous acid. It also increases the average hydroxyl radical and ozone by 10% and 1.7 ppbv, respectively.

Keywords Emissions, heterogeneous reaction, nitrous acid, surface photolysis reaction

1. Introduction

The importance of nitrous acid (HONO) chemistry in producing hydroxyl (OH) and hydroperoxy (HO₂) radicals is well established. Alicke et al. (2002, 2003) suggested that the photolysis of HONO may provide as much as 34% of daily integrated OH levels. Zhou et al. (2002) reported that the photolysis of HONO may produce up to 24% of the total daily radical production. Using concurrently measured HONO and OH at the Meteorological Observatory Hohenpeissenberg in summer 2002 and 2004, Acker et al. (2006) suggested that the photolysis of HONO produced 42% of the integrated photolytic HO_x (OH + HO₂) formation. While the effect of HONO on OH is established, the chemical reactions producing HONO are not well understood. Most air quality models, including the Community Multiscale Air Quality (CMAQ) modeling system, employ only homogeneous chemical reactions for HONO. Recent studies suggest that emissions, heterogeneous reactions, and surface photolysis of adsorbed nitric acid may produce additional HONO in the atmosphere (Vogel et al., 2003; Zhou et al., 2003). In this study, the effects of these sources on HONO are evaluated using the CMAQ modeling system.

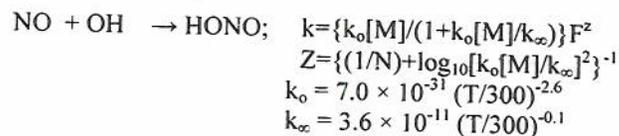
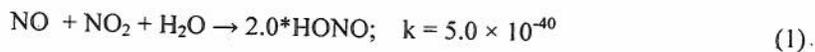
2. Methodology

2.1. Model description

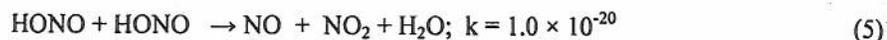
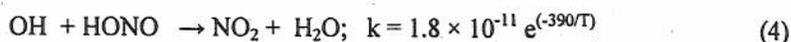
Model simulations were performed using the CMAQ modeling system (version 4.6) (Binkowski and Roselle, 2003; Byun and Schere, 2006). The CMAQ chemical transport model was configured to use the mass continuity scheme to describe advection processes, the Asymmetric Convective Model version 2 (ACM2) (Pleim, 2007) to describe vertical diffusion processes, the multiscale method to describe horizontal diffusion processes, an adaptation of the ACM algorithm for convective cloud mixing, and the Carbon Bond (CB05) mechanism to describe the gas-phase chemical mechanism (Yarwood et al., 2005; Sarwar et al., 2007). Aqueous chemistry, aerosol processes, and dry and wet deposition were also included. The meteorological driver for the CMAQ modeling system was the PSU/NCAR MM5 system version 3.5 (Grell et al., 1994). Predefined clean air vertical profiles for initial and boundary conditions provided in the CMAQ modeling system were used. Model simulations were performed for July 2001; the model was spun up for seven days to minimize the effect of initial conditions on predictions.

2.2. HONO chemistry

The CB05 mechanism contains five homogeneous reactions related to HONO (Yarwood et al., 2005). These reactions and their rate constants are shown in Eqs. (1)–(5) (NO = nitric oxide, NO₂ = nitrogen dioxide, H₂O = water vapor, k = expression for rate constant, first order rate constants are in units of second⁻¹, second order rate constants are in units of cm³ molecule⁻¹ second⁻¹, third order rate constants are in units of cm⁶ molecule⁻² sec⁻¹, T = temperature in Kelvin, M = the total pressure in molecules/cm³, photolysis rate for Eq. (3) is at 40° N (typical summer noon). While this study used the CB05 mechanism, the chemical reactions used in other widely used atmospheric chemical mechanisms are also similar. For example, the CB-IV mechanism contains the same five chemical reactions for HONO (Gery et al., 1989). The Statewide Air Pollution Research Center (SAPRC-99) mechanism contains four chemical reactions for HONO (Eqs. (2)–(4) and an additional photolytic reaction) (Carter, 2000).

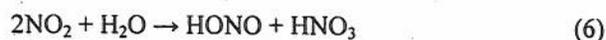


$$F = 0.6 \text{ and } N = 1.0 \quad (2)$$



As shown below, CMAQ predictions with observed data indicate incorporating only the homogeneous reactions results in HONO predictions that are seriously deficient. HONO emissions are currently not included in the CMAQ modeling system. Several investigators have reported HONO emissions from motor vehicles (Winer and Biermann, 1994; Kirchstetter et al., 1996; Kurtenbach et al., 2001). Kirchstetter et al. (1996) measured HONO and NO_x emissions from on-road vehicles at Caldecott Tunnel in San Francisco, California and reported a value of 2.9×10^{-3} for the HONO/NO_x emissions ratio. Kurtenbach et al. (2001) conducted measurements in the Wuppertal Kiesbergtunnel and reported a value of 8×10^{-3} for the same ratio. Winer and Biermann (1994) also reported a value of 8×10^{-3} for the same ratio. For this study, HONO emissions were estimated using a value of 8×10^{-3} for the HONO/NO_x emissions ratio for on-road and off-road vehicles.

Several heterogeneous reactions have been suggested to produce HONO formation in the atmosphere (Aumont et al., 2003). However, most of these reactions appear to be not significant for HONO production in the atmosphere. The heterogeneous reaction involving NO₂ and H₂O has been shown to be important for HONO production in the atmosphere (Vogel et al., 2003):



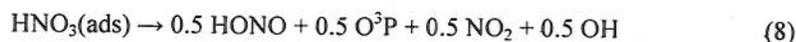
Laboratory studies suggest that reaction (6) is first order in NO₂ (Finlayson-Pitts and Pitts, 2000) and can occur on aerosol and ground surfaces. This heterogeneous reaction is implemented into the CMAQ modeling system with a rate constant of $3.0 \times 10^{-3} \times \text{S/V m}^{-1}$ following Kurtenbach et al. (2001) (S/V is the ratio of surface area to volume of air). The reaction can occur on aerosol as well as ground surfaces. Aerosol surface areas are generally smaller than ground surface areas; thus aerosol surface areas are less effective in producing HONO in the atmosphere. Ground surface areas provided by leaves can be estimated using the Leaf Area Index (LAI). Jones (2006) suggests that the use of LAI underestimates leaf surface areas by at least a factor of two since it only accounts for areas on one side of the leaves. Thus, the S/V ratios for leaves were estimated as follows:

$$\text{S/V} = 2 \cdot \text{LAI} / \text{surface layer height} \quad (7)$$

Buildings and other structures can also enhance ground surface areas in urban environments. However, estimates of these areas are not readily available. In the absence of such information, an ad hoc approach was used to estimate the ground surface areas for buildings and other structures in urban environments. Svensson

et al. (1987) studied the kinetics of the reaction involving NO_2 and H_2O and suggested a value of 0.2 m^{-1} for typical urban environments. They, however, also indicated that some building materials may provide an order of magnitude greater surface area than their simple projected surface areas due to porosity and roughness. For this study, the S/V ratio for buildings and other structures at the grid-cell with the highest urban environment was assigned a value of 0.3 m^{-1} . The S/V ratios for buildings and other structures for other urban environments were linearly scaled to this S/V ratio by assuming that the values are proportional to the percent urban area in any grid-cell. Using this procedure, the total S/V ratio for the grid-cell containing northeast Philadelphia was estimated to be 0.28 m^{-1} , which is almost 5 times lower than the value of 1.3 m^{-1} used by Cai et al. (2007) for New York. HONO produced via the heterogeneous reaction on ground surfaces was released into the first layer of the model.

Several recent studies also suggest the possibility of the production of HONO via surface photolysis (Zhou et al., 2002, 2003; Vogel et al., 2003; Acker et al., 2006). In their study, Vogel et al. (2003) used a hypothetical species to add a source for HONO production in the surface layer of the model via photolysis since the species that may undergo photolysis to produce HONO was not known. Zhou et al. (2003) recently conducted laboratory experiments and suggested that adsorbed nitric acid (HNO_3) on surfaces can undergo photolysis to produce HONO and NO_2 . A photolysis reaction producing HONO and NO_2 was added to the CMAQ modeling system (Eq. (8)) by assuming that the adsorbed amount is equal to the HNO_3 deposited via dry deposition since the last precipitation (O^3P = ground state oxygen atom).



Zhou et al. (2003) reported a photolysis rate of $1.3 \times 10^{-3} \text{ minute}^{-1}$ at noontime tropical condition for the surface photolysis of adsorbed HNO_3 , which is 24 times greater than the gaseous HNO_3 photolysis rate in the CMAQ modeling system. The surface photolysis rate of adsorbed HNO_3 was scaled to the photolysis rate of gaseous HNO_3 used in the CMAQ modeling system. HONO and NO_2 produced via the surface photolytic reaction was released into the first layer of the model only.

2.3. Observed data

Model predictions are compared with measurements from the Northeast Oxidant and Particle Study conducted at northeast Philadelphia (<http://lidar1.ee.psu.edu>) in July 2001. Continuously measured data from the study were converted into hourly averaged data which were used to calculate an average diurnal profile. Average values for night and day were calculated using the average diurnal profile.

3. Results

Four different model simulations were performed as shown in Table 1.

Table 1 Summary of cases investigated.

Case	Emissions Included	Chemical mechanism used
A	NO _x , SO ₂ , CO, VOC, NH ₃ , aerosol	CB05
B	NO _x , SO ₂ , CO, VOC, NH ₃ , aerosol, HONO	CB05
C	NO _x , SO ₂ , CO, VOC, NH ₃ , aerosol, HONO	CB05 + reaction 6
D	NO _x , SO ₂ , CO, VOC, NH ₃ , aerosol, HONO	CB05 + reaction 6 and 8

The average predicted and observed HONO at northeast Philadelphia are presented in Table 2. Observed HONO mixing ratio was 50% greater at night than that during the day. Predicted HONO mixing ratio for the case A was only 0.01 ppbv at night compared to an observed value of 1.26 ppbv. Contrary to the observed data, predicted HONO mixing ratio was greater during the day by at least a factor of 4 over the mixing ratio at night. Predicted HONO mixing ratio was significantly lower than the observed data both at night and during the day.

Table 2 Summary results.

Case	Night			Day		
	Obs. HONO (ppbv)	Pred. HONO (ppbv)	Obs./ pred. (ratio)	Obs. HONO (ppbv)	Pred. HONO (ppbv)	Obs./ Pred. (ratio)
A	1.26	0.01	126	0.85	0.04	21
B	1.26	0.11	11	0.85	0.07	12
C	1.26	0.95	1.3	0.85	0.25	3.4
D	1.26	0.96	1.3	0.85	0.60	1.4

When HONO emissions were added to the model (case "B"), predicted HONO reached to 0.11 ppbv at night and was slightly higher at night than during the day. Predicted HONO mixing ratio was still lower than the observed data by a large margin both at night and during the day.

When the heterogeneous reaction was also added to the model (case "C"), predicted HONO mixing ratio further improved at night and reached to within 30% of the observed data. However, predicted HONO mixing ratio was still lower than the observed data during the day by a factor of 3.4.

When the surface photolysis of adsorbed HNO₃ was added to the model (case "D"), predicted HONO mixing ratio improved to 0.60 ppbv during the day due to the increased HONO production and reached to within 40% of the observed data.

The observed ratio of HONO/HNO₃ was 2.9 at night. For the case A, the ratio was only 0.006 and improved to 0.6 for the case D. During the day, the observed ratio was 0.73 compared to a value of only 0.02 for the case A. It improved to 0.2 for the case D.

The relative contribution of these production pathways to predicted HONO for the case D is dominated by two pathways. The reaction #6 contributed 56% to the predicted HONO and was the largest contributor. The reaction #8 was the second

largest contributor and contributed 32% to the predicted HONO. The HONO emissions and the homogeneous reactions (Eqs. (1)–(5)) contributed only 8% and 4% to the predicted HONO, respectively.

HONO undergoes photolysis in the atmosphere to produce OH radicals. The additional HONO enhanced the average OH by 10% in the case D compared to that of the case A. The inclusion of the additional HONO sources increased the average O_3 by 1.7 ppbv. The increased O_3 is a contribution of additional VOC oxidation via enhanced OH as well as the photolysis of additional NO_2 generated from the surface photolysis of adsorbed HNO_3 (reaction #8).

4. Summary

The results of this study suggest that heterogeneous reaction and surface photolysis of adsorbed HNO_3 are important sources of HONO in the atmosphere. Most air quality models, however, do not currently account for these sources; thus, models tend to under-predict HONO by a large margin. The incorporation of these sources improves HONO predictions. The improved HONO predictions can increase OH as well as O_3 . Surface areas of leaves can be estimated using the LAI. Better estimates of the surface areas of buildings and other structures in urban environments are needed to improve HONO predictions via the heterogeneous reaction. However, such information is not readily available; efforts should be directed in determining such values. The surface photolysis of adsorbed HNO_3 producing HONO and NO_2 during the day is an emerging topic; many related issues are still unknown. However, it appears to provide the missing HONO source during the day without which model predictions remain under-predicted compared to observed data. Thus, this reaction should be further explored in laboratory as well as field studies before it can be confidently used in air quality models.

Disclaimer The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

References

- Acker K, Möller D, Wiprecht W, Meixner FX, Bohn B, Gilge S, Plass-Dülmer C, Berresheim H (2006) Strong daytime production of OH from HNO_2 at a rural mountain site, *Geophys. Res. Lett.*, 33, L02809, doi:10.1029/2005GL024643.

- Alicke B, Platt U, Stutz J (2002) Impact of nitrous acid photolysis on the total hydroxyl radical budget during the limitation of oxidant production/Pianura Padana Produzione di Ozono study in Milan, J. Geophys. Res., 107, doi:10.1029/2000JD000075.
- Alicke B, Geyer A, Hofzumahaus A, Holland F, Konrad S, Pätz HW, Schäfer J, Stutz J, Volz-Thomas A, Platt U (2003) OH formation by HONO photolysis during the BERLIOZ experiment, J. Geophys. Res., 108, 8247, doi:10.1029/2001JD000579.
- Aumont B, Chervier F, Laval S (2003) Contribution of HONO sources to the NO_x/HO_x/O₃ chemistry in the polluted boundary layer, Atmos. Environ., 37, 487–498.
- Binkowski FS, Roselle SJ (2003) Community Multiscale Air Quality (CMAQ) model aerosol component, I: Model description, J. Geophys. Res., 108(D6): 4183, doi:10.1029/2001JD001409.
- Byun D, Schere KL (2006) Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system, Appl. Mech. Rev., 59, 51–77.
- Cai C, Hogrefe C, Schwab JJ, Katsafados P, Kallos G, Ren X, Brune WH, Zhou X, He Y, Demerjian KL (2007) Performance evaluation of an air quality forecast modeling system for a summer and winter season – Part II: HONO formation processes and their implications for HO_x budgets, J. Geophys. Res., in review.
- Carter, WPL (2000) Implementation of the SAPRC-99 chemical mechanism into the Models-3 Framework, report to the United States Environmental Protection Agency. Available at <http://www.cert.ucr.edu/~carter/absts.htm#s99mod3>
- Finlayson-Pitts BJ, Pitts JN Jr (2000) Chemistry of the Upper Lower Atmosphere, Theory, Experiments and Applications, Academic, San Diego, CA.
- Gery MW, Whitten GZ, Killus JP, Dodge MC (1989) A photochemical kinetics mechanism for urban and regional scale computer modeling. J. Geophys. Res., 94(D10), 12925–12956.
- Grell G, Dudhia J, Stauffer D (1994) A description of the fifth-generation Penn State/NCAR Mesoscale model (MM5), NCAR Tech. Note NCAR/TN-398+STR.
- Jones MR (2006) Ammonia deposition to semi-natural vegetation, PhD dissertation, University of Dundee, Scotland.
- Kirchstetter TW, Littlejohn D (1996) Measurements of nitrous acid in motor vehicle exhaust, Environ. Sci. Technol., 30, 2843–2849.
- Kurtenbach R, Becker KH, Gomes JAG, Kleffmann J, Lorzer JC, Spittler M, Wiesen P, Ackermann R, Geyer A, Platt U (2001) Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, Atmos. Environ., 35, 3385–3394.
- Pleim JE (2007) A combined local and nonlocal closure model for the atmospheric boundary layer. part I: model description and testing, J. Appl. Meteor. Clim., 46, 1383–1395.
- Sarwar G, Luecken V, Yarwood G, Whitten G, Carter WPL (2007) Impact of an updated carbon bond mechanism on predictions from the Community Multiscale Air Quality (CMAQ) modeling system: preliminary assessment, J. Appl. Meteor. Clim., accepted.

- Svensson R, Ljungstrom E, Lindqvist O (1987) Kinetics of the reaction between nitrogen dioxide and water vapour, *Atmos. Environ.*, 21, 1529–1539.
- Vogel B, Vogel H, Kleffmann J, Kurtenbach R (2003) Measured and simulated vertical profiles of nitrous acid – Part II, model simulations and indications for a photolytic source, *Atmos. Environ.*, 37, 2957–2966.
- Winer AM, Biermann HW (1994) Long pathlength differential optical absorption spectroscopy (DOAS) measurements of gaseous HONO, NO₂ and HCHO in the California South Coast Air Basin. *Res. Chem. Intermed.*, 20, 423–445.
- Yarwood G, Rao S, Yocke M, Whitten G (2005) Updates to the Carbon Bond Chemical Mechanism: CB05, Final Report to the US EPA, RT-0400675, Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf
- Zhou X, Civerolo K, Dai H, Huang G, Schwab JJ, Demerjian KL (2002) Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State, *J. Geophys. Res.*, 107(D21), 4590, doi:10.1029/2001JD001539.
- Zhou X, Gao H, He Y, Huang G, Bertman SB, Civerolo K, Schwab J (2003) Nitric acid photolysis on surfaces in low-NO_x environments: significant atmospheric implications, *Geophys. Res. Lett.*, 30(23), 2217, doi:10.1029/2003GL018620.

Discussion

A. Venkatram:

How do you adsorb HNO₃ in the model? How do you justify assuming that all the day deposited HNO₃ is available for photolysis? Does the inclusion of HNO₃ photolysis affects HNO₃ in the atmosphere?

G. Sarwar:

In the model, it is assumed that HNO₃ that is removed from the atmosphere via dry deposition gets adsorbed on surfaces. Adsorbed HNO₃ can then undergo photolysis to produce HONO during the day. A fraction of the deposited HNO₃, indeed, may not be available all day for photolysis. However, the detailed processes that form HONO in the atmosphere are still unknown. In this study, we explored the effects of heterogeneous reaction, homogeneous reactions, emissions, and surface photolysis of HNO₃ on HONO. Since we used all available adsorbed HNO₃ for photolysis, it does represent the upper limit of HONO formed via the surface photolysis process. The inclusion of surface photolysis of adsorbed HNO₃ did not significantly affect HNO₃ in the atmosphere.

W. Gong:

Did the changes involving HONO make any difference in model predictions of O₃?

G. Sarwar:

The changes involving HONO made some differences in ozone predictions. Predicted ozone increased by up to 2.4 ppbv. The diurnally averaged ozone increased by 1.4 ppbv. The increases started during the morning hours and continued throughout the day. However, the increases in predicted ozone were not adequate to explain the observed early morning rise.

M. Brauer:

How was HONO measured in the field campaign? Depending on the measurement approach there may be artifacts from other nitrogen species.

G. Sarwar:

Ambient HONO were measured using ion chromatography technique that has a detection limit of about 0.11 pptv and accuracy of about 5%.

