THE CYCLING OF NITROUS ACID (HONO) IN THE AMBIENT AIR

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1. INTRODUCTION

Night-time reactions to form nitrous acid (HONO) were studied, using ambient measurements collected at the Pittsburgh Air Quality Study (PAQS) from July 2001 to September 2002. HONO is a significant morning-time source of hydroxyl (•OH) radicals which drive reactions to form smog. Smog has public health and public welfare concerns. The formation of HONO is poorly understood, an issue which has limited the ability of air quality models to predict the effect of emissions reductions on ambient air quality. This research draws upon an unprecedented data set to reveal the role of HONO in night-time chemistry.

Objective: Characterize the Formation of HONO
• Develop a box model that uses measurements of meteorology and NOx, HNO3, and O3 as inputs.
• Use ambient measurements to estimate kinetic parameters of significance to HONO formation.
• Evaluate reaction pathways proposed in the literature by comparing ambient measurements to model predictions, and use to propose more robust reaction schemes.

2. BACKGROUND

Sources of Nitrous Acid:
• Direct emission from combustion processes
• Homogeneous reaction of NO with •OH
• Heterogeneous reaction of NO2 with water vapor

HONO has a Diurnal Cycle in the Atmosphere:
• HONO concentration is near-zero during the day, because any HONO that is emitted or formed is quickly photolyzed to NO and •OH.
• HONO concentrations gradually build overnight, as photolysis does not occur.
• Come sunrise, HONO that built up overnight is quickly photolyzed, releasing a burst of •OH.

The Cycle of Nitrogen Oxides and Ozone

The Missing Link:
• While homogeneous reactions to form HONO are well understood, they do not explain the amount of HONO observed at night.
• Heterogeneous reactions may be the missing link, although they have only been observed experimentally.
• Observed kinetics depend on the surface-to-volume ratio, which indicates a heterogeneous reaction. Observations also suggest the reaction is first order in NOx, and in water vapor.

\[ 2\text{NO}_x + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]

Rate constant: \[ k_{iilies} = 3 \times 10^{-3} \text{ mmol m}^{-3} \text{ s}^{-1} \]
Reaction probability: \[ \gamma = 10^{-6} \]

3. AMBIENT MEASUREMENTS

The literature suggested that HONO formation depends on temperature and requires the presence of wet surface layer on atmospheric particles. As a result, we selected six periods of study from the PAQS dataset to represent various temperatures (summer vs winter) and amount of particles and water vapor in the air.

PAQS Measurements to be Used in the Analysis:
• Meteorology: Rainfall, wind speed and direction, temperature, UV solar radiation, and relative humidity
• Gas species concentrations: NO, NO2, HONO, HNO3, and O3
• Particle features: Mass, size, organic and inorganic composition
• Fog: Organic and inorganic composition

Features of Selected Periods of Study:
• No precipitation - HONO is easily removed by wet deposition
• Low wind speed - HONO observations are minimally affected by upwind anthropogenic sources
• Stable relative humidity - HONO formation is more constant
• Data availability

4. ANALYSIS OF THE SELECTED DAYS

A strong diurnal cycle of HONO is observed. HONO mixing ratio increases steadily after sunset and reaches a maximum value just after midnight.

The rate of HONO formation at night, calculated using ambient observations, is consistent with the heterogeneous reaction probability measured in the controlled laboratory setting.

6. FUTURE WORK

Work to date suggests that the heterogeneous reaction of NO2 and H2O is the major source of HONO in the atmosphere.
• Develop the box model from the mass balances on each chemical that participates in the HONO chemistry and calculate rate constants for each chemical from the ambient measurements (as shown for HONO).
• Run the model, using ambient measurements as starting conditions.
• Compare predicted changing concentration of HONO to observations.
• Quantify the impact of HONO photolysis on early morning •OH formation.