Auxiliary Mechanisms (Wall Models) for UNC Outdoor Chamber

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Abstract

It has been recognized for more than 30 years that the walls of "smog chambers" provided sites for heterogeneous reactions that influenced the outcome of the homogeneous gas phase reactions. In the early 1980's several efforts were made to elucidate the origins of these effects, with most attention focused on the heterogeneous formation of nitrous acid (HONO) which was subsequently released into the gas phase. While these efforts effectively demonstrated that most likely HONO was being formed, actual mechanisms and process rates for this phenomena have not been developed for chambers. Instead a small set of un-real or parameterized reactions have been used to approximate the HONO formation based upon "characterization experiments." These experiments have included the simplest type of experiments, i.e., NO_x/CO, NO_x/CH_4, and NO_x/n-butane experiments. The basic conceptual model has been that the gas phase chemistries of these simple systems are so well understood, that any failure of a reaction mechanism simulation to reproduce the observations from these experiments was due to chamber wall processes or chamber-dependent initial conditions. These chamber-dependent conditions included unintended creation of initial HONO due to injection of the initial NO_x from high concentration sources. Such chamber-dependent reactions and inputs have often been expressed as "Auxiliary Mechanisms," one for each chamber to be simulated. When testing or evaluating a reaction mechanism in a given chamber, a chamber-dependent mechanism is combined with a "Principle (or Core) Mechanism," which is asserted to be chamber-independent. Obviously mistakes or misrepresentations in the auxiliary mechanism can introduce compensating errors in the principle or core mechanism.

Measurements in the UNC outdoor chamber and laboratory work in Europe have shown that the simple ideas used in our Auxiliary Mechanisms are not valid. In most modeling evaluations in the US, it has been assumed that some initial amount of HONO (2 to 5 ppb) was created in the chambers due to injection, and that during the experiment, NO_2 was converted to HONO at a rate proportional to the product of the radiation intensity and a "radical source" scale factor.

The chamber HONO measurements show that initial HONO is very low in the UNC chambers (< 0.5 ppb) and that its mixing ratio increases during the experiment, reaching a maximum sometime between NO-to-NO_2 cross-over and just after NO_2 maximum.

Recent laboratory work at Wuppertal, Germany has shown that HONO formation in systems with NO_2 and water vapor present is initially first order in NO_2 gas phase concentration and that the yield is essentially 0.5. This is consistent with $NO_2 + NO_2 + H_2O \longrightarrow HONO + HNO_3$, all in aqueous solution, where the rate determining step is NO_2 partitioning to the aqueous phase. Furthermore, they have shown that as the reaction proceeds, the HONO production decreases and that N_2O is created instead of HONO. The mechanistic explanation offered was that the increasing acidity of the aqueous solution leads to the creation of the NO^+ ion, which then oxidizes HONO to N_2O before HONO can partition out of the aqueous solution. The concept that the "wall source" of HONO might be shut off due to a high acidity provided a major shift in our ideas of how an auxiliary mechanism must be formulated. We have created several new auxiliary mechanisms based on these ideas.

In simulating NO_x/CO experiments, it became clear that such experiments were far from ideal in "characterizing" the chamber wall source. This is because the only gas-phase sink for NO_x in such experiments is the formation of HONO via $\cdot OH + NO$, or the formation of HNO_3, either via $\cdot OH + NO_2$ or via $O_3 + NO_2$ leading to N_2O_5, which hydrolyzes to HNO_3. At the beginning of the experiment, HONO is the only source of new radicals (and the source of the HONO is NO_2 reacting with wall water), but once O_3 formation starts, the photolysis of O_3 becomes the major source of new $\cdot OH$, and the formation of N_2O_5 provides an additional strong source of HNO_3. Analysis of the simulation mechanism shows that by the time O_3 formation starts, a significant amount of HNO_3 has already been formed and much of this has partitioned to our chamber walls. It appears that shortly after O_3 formation begins, the wall source of HONO must be quenched or an excess of $\cdot OH$ radicals is introduced into the system. Three sets of HONO measurements in NO_x/CO experiments indicate that most HONO production stops just after O_3 formation occurs.

While we were able to formulate a relative simple set of gas to aqueous phase partitioning reactions and aqueous-phase reactions to create HONO which gave excellent simulations of the initial NO oxidation rates and NO_2 production rates, with-out a full acid-base, redox reaction set in the aqueous phase, we could not satisfactorily simulate the rapid termination of $HONO$ production, thus, we consistently overpredicted the O_3 formed in these systems.

The next step is to create a fully explicit aqueous phase, weak and strong solution chemistry mechanism for nitrogen oxides and to couple this chemistry to the usual gas-phase chemistry. This system will provide more testable hypotheses in chamber experiments which can then lead to a refinement in the wall-mediated mechanisms. Additional measurements have already been suggested, for example, we intend to measure N_2O levels in new NO_x/CO experiments, as well as trying to assess the pH of the wall water film or to measure conductivity of the Teflon film inside the chamber.

One insight already gained is that the use a particular type of chamber experiment to derive a "chamber characterization" is clearly not a valid concept, as the actual time series of HNO_3 formation would have a strong effect on the $HONO$ production rate from the walls. In subsequent experiments, a different time series of HNO_3 would result in a different rate of $HONO$ production than that represented by the "parameterized" un-real reactions used in the simulations.

On the other hand, an understanding of nitrogen wall chemistry processes could lead to a "chamber cleaning" procedure that might result in a much smaller experiment to experiment carry over effect.

In summary we offer two puns:

> Acid not what your walls do to your gases,
> Acid what your gases do to your walls.

and

> Too acid, or not too acid, that is the question.