

RELATIVE IMPORTANCE OF THE PRODUCTION AND DESTRUCTION OF
CHEMICALLY REACTIVE SPECIES IN DEEP CONVECTIONMary C. BarthNational Center for Atmospheric Research
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1. INTRODUCTION

Deep convection affects the distribution of tropospheric constituents in many ways. Insoluble chemical species are transported from the boundary layer to the upper troposphere in the convective core. Highly soluble species are scavenged by the cloud drops and are precipitated to the surface.

In tropospheric chemistry, ozone (O_3) concentrations and the formation and loss of ozone are of particular interest because of the critical role ozone has on our environment. Ozone is controlled by nitrogen oxides ($NO_x = NO + NO_2$) and hydrogen oxides ($HO_x = OH + HO_2$). In the upper troposphere it has been learned that the injection of HO_x precursors such as peroxides and aldehydes from convection can substantially contribute to the HO_x reservoir and potentially affect ozone concentrations (Prather and Jacob, 1997). However there has been little work done to examine the fate of HO_x precursors while in the convective environment. To determine the importance of microphysics and chemistry on two HO_x precursors, hydrogen peroxide (H_2O_2) and formaldehyde (CH_2O) during transport through convective cores, an examination of numerical model results that represent the dynamics, microphysics and chemistry in and around a midlatitude deep convective storm is performed.

2. CHEMICAL PRODUCTION AND
DESTRUCTION OF H_2O_2 AND CH_2O

The primary source for H_2O_2 in the gas phase is the self reaction of hydroperoxy radical (HO_2). In clear air, H_2O_2 is destroyed by either photodissociation to form hydroxyl radical (OH) or by reaction with OH to form HO_2 . H_2O_2 is very soluble so that in the vicinity of cloud drops much of the H_2O_2 dissolves into the drops. In the cloud drops, H_2O_2 reacts mostly with bisulfite ion (HSO_3^-) to form sulfate, but also can react with OH. H_2O_2 is formed by the aqueous chemical reaction of HO_2 reacting with its dissociated form (O_2^- , superoxide).

With moderate NO_x concentrations (~ 500 pptv in the boundary layer to 10s of pptv in the free

troposphere), CH_2O is formed by the reaction of methyl peroxy radical CH_3OO and NO in the gas phase. The primary CH_2O loss reactions are photodissociation and reaction with OH in the gas phase. When CH_2O dissolves into cloud drops it immediately hydrates and is not susceptible to in-cloud photolysis, but it does rapidly react with aqueous OH to form formic acid. Production of CH_2O in cloud and rain drops via OH oxidation of methyl peroxide is quite small compared to its gas-phase production.

While H_2O_2 and CH_2O are transported by the convective motions, the fraction residing in the cloud and rain water can undergo transfer among the hydrometeor reservoirs (cloud water, rain, ice, snow, hail). The dissolved species is also subject to removal by precipitation (in snow and hail, but ultimately to the surface in rain drops).

3. PROCEDURE

Results from numerical simulations of convection and chemistry can be analyzed to determine the relative importance of the production and loss of each chemical species. For this analysis, the simulations performed with a convective cloud model coupled with chemistry (Skamarock et al., 2000; Barth et al., 2000, 2001) represent the July 10, 1996 STERAO midlatitude summer thunderstorm that evolved from a multicellular storm to a quasi-supercell. For this paper the processes occurring during the multicellular stage of the storm are discussed.

To examine the effect of ice microphysics on the distribution of chemical species, two simulations are performed. For the first simulation the soluble species is degassed from the liquid phase during freezing. In the second simulation, the soluble species is retained in the frozen drop and is subjected to the same microphysical processes and sedimentation as the snow or hail particle. The rates of formation and destruction are examined of two HO_x precursors, H_2O_2 and CH_2O , in the cloud water and rain regions of the storm. In addition the chemical production and loss in the gas-phase, cloud water, and rain of these two species are discussed.

In the total model domain, gas-phase processes dominate because there are more clear-air grid

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points than cloudy grid points. By sampling just the cloud water and rain regions the effects of aqueous chemistry are maximized. The transport of air from the boundary layer to the upper troposphere coincides with the cloud water region, thus the results presented below show what processes affect H_2O_2 and CH_2O as these species are lifted to the upper troposphere.

To compare the relative importance of the sources and sinks of H_2O_2 and CH_2O , each source or sink is summed at each model level at locations where the cloud water or rain exist producing profiles of the total rate of the process. These profiles are then combined to show the net production of H_2O_2 or CH_2O for (a) microphysical processes, (b) mass transfer between gas and aqueous phases (termed dissolution), (c) chemistry, and (d) sedimentation.

4. RESULTS

4.1 Hydrogen Peroxide

The net microphysics, dissolution, and chemical production of H_2O_2 in the cloud water is shown in Figure 1 for both simulations (retention of the species during freezing of drops, and degassing of the species during freezing of drops). The production and destruction of H_2O_2 in the cloud water is dominated by the transfer of H_2O_2 into and out of the cloud drops. Most of the transfer into the drops occurs near and above cloud base (especially for the simulation where H_2O_2 is degassed during freezing processes). At mid to upper levels of the convective core, the transfer of H_2O_2 out of the cloud drops to the rain (near 3 km), snow and hail (above 3 km) is important. The removal of H_2O_2 (cw) by microphysics is accomplished by the larger particles accreting the cloud water. Note, for the simulation in which the soluble species is degassed during freezing processes such as riming, that the species is transferred to the gas phase. Compared to the dissolution and microphysical transfer of H_2O_2 , chemistry in the cloud drops is quite small.

The destruction of H_2O_2 in the rain (Figure 2) is controlled by the sedimentation of rain drops. This is especially true for the simulation in which H_2O_2 was retained in the snow or hail during freezing, because much of the H_2O_2 in rain is a result of melting snow and hail rather than accretion of cloud drops (besides dissolution from the gas phase, the only source of H_2O_2 (r) is from cloud water for the simulation in which the soluble species is degassed during freezing). Because of the larger source of H_2O_2 (r) for the simulation in which the soluble species is retained during freezing, a larger sink via rain out is expected. Transfer of H_2O_2 in and out of the rain and aqueous chemistry in the rain is negligible compared to the sedimentation and microphysical transfer.

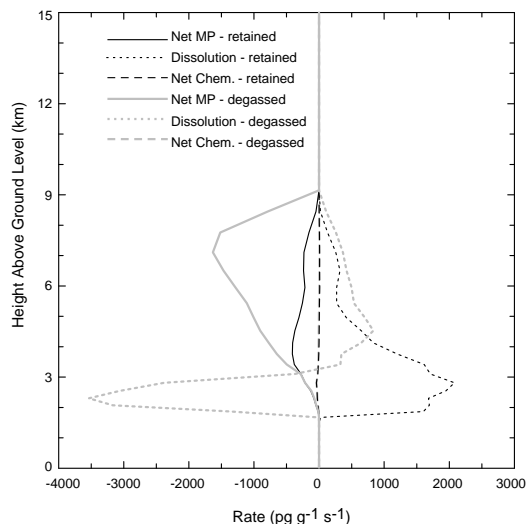


Figure 1. Sources and sinks of H_2O_2 (cw). Black lines are for the simulation in which soluble species are retained in the frozen particle during freezing processes. Gray lines are for the simulation in which soluble species are degassed during freezing. Solid lines are total microphysical processes, dotted lines are transfer between gas and aqueous phases via dissolution, dashed lines are chemical processes.

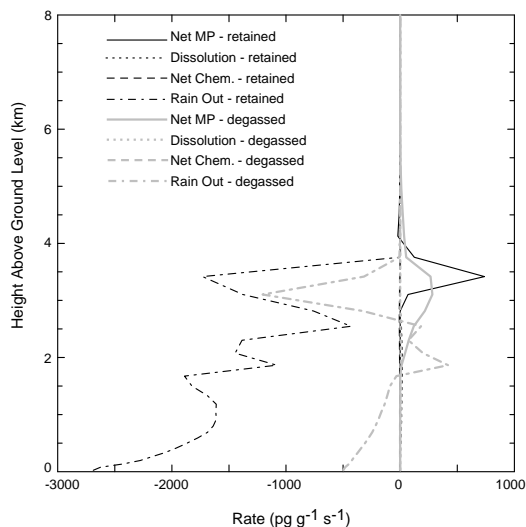


Figure 2. As in Figure 1, but for H_2O_2 (r). Dash-dotted lines are sedimentation in rain.

The net chemical production of H_2O_2 (Figure 3) indicates that the chemical sources and sinks tend to balance each other. For example, the gas-phase formation reaction of $\text{HO}_2 + \text{HO}_2$ reaches values over $100 \text{ pg g}^{-1} \text{ s}^{-1}$, but the net production is reduced by H_2O_2 photodissociation and oxidation by OH radical, which reach values of 45 and $40 \text{ pg g}^{-1} \text{ s}^{-1}$, respectively. In the cloud water, the $\text{HO}_2 + \text{O}_2^-$ reaction produces up to $25 \text{ pg g}^{-1} \text{ s}^{-1}$ of H_2O_2 to balance, in part, the destruction of H_2O_2 by reaction with HSO_3^- (up to $65 \text{ pg g}^{-1} \text{ s}^{-1}$). While H_2O_2 (cw)

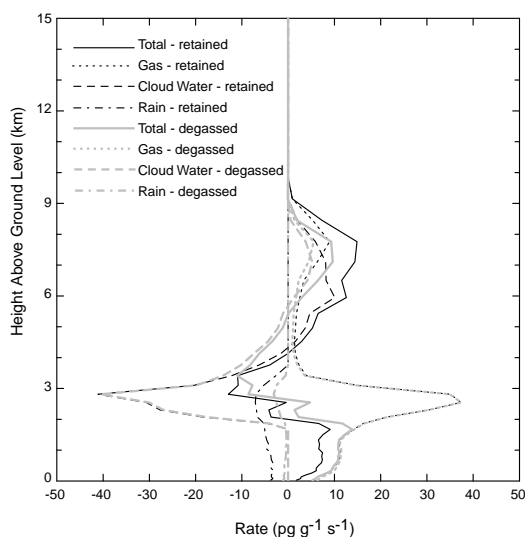


Figure 3. Chemical sources and sinks of H_2O_2 . Solid lines are for the total (gas + cloud water + rain) species. Dotted lines are for the species in the gas phase. Dashed lines are for the species in the cloud water, and dash-dotted lines are for the species in rain. Definitions of black and gray lines are given in Figure 1.

is destroyed in the lower part of the cloud water core by reaction with HSO_3^- , it is produced in the upper cloud water region by $\text{HO}_2 + \text{O}_2^-$. This production of H_2O_2 may increase the expected amount of H_2O_2 transported to the upper troposphere. In addition there is an increased amount of gas-phase production of H_2O_2 near the top of the convective core.

4.2 Formaldehyde

As was the case with H_2O_2 , the net production of cloud water CH_2O (Figure 4) is dominated by the transfer of CH_2O into and out of the cloud drops especially near cloud base. At mid to upper levels of the cloud water region, the transfer of CH_2O out of the cloud water by microphysical processes is important. The chemistry of CH_2O in the cloud water is negligible compared to these physical processes.

The net production of CH_2O (r) (Figure 5) is dominated by the removal of CH_2O (r) by sedimentation, particularly for the simulation in which the soluble species is retained in the frozen hydrometeor during freezing processes. As with H_2O_2 , the primary source of CH_2O in the rain comes from melting snow and hail for the simulation in which the CH_2O is retained in the frozen hydrometeor during freezing and from collecting cloud drops for the simulation in which the CH_2O is degassed during the freezing process. Again, the chemistry in the rain is quite small compared to the physical processes.

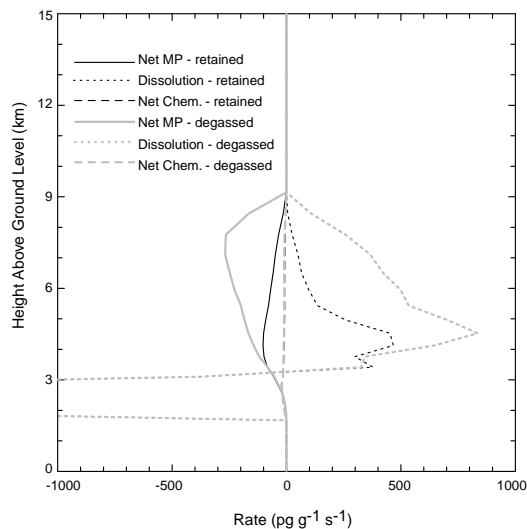


Figure 4. Same as Figure 1, but for CH_2O (cw).

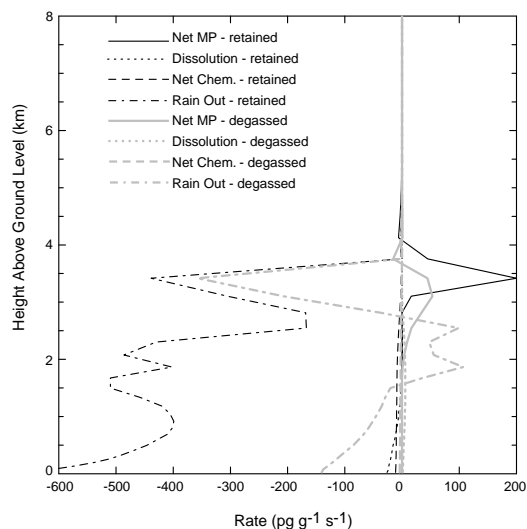


Figure 5. Same as Figure 2, but for CH_2O (r).

The net chemical production of CH_2O (Figure 6) is controlled by the gas-phase destruction reactions (photodissociation of CH_2O and oxidation of CH_2O with OH) below the 4 km height. Near cloud base, aqueous-phase reaction of CH_2O with OH accounts for 15–20% of the total destruction. In the mid to upper cloud water region aqueous-phase chemistry plays a more important role to the chemical destruction of CH_2O . The gas-phase chemistry in the upper cloud water region differs between the two simulations performed. Because CH_2O is degassed in this region for the simulation in which the species is degassed during freezing, its gas-phase destruction is greater than its gas-phase production by the reaction of NO and CH_3OO . For the simulation for which the species is retained in the frozen hydrometeor, there is hardly any gas-phase destruction of

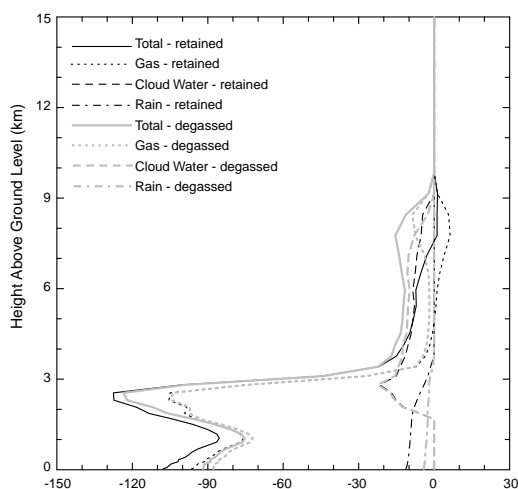


Figure 6. Same as Figure 3, but for CH_2O .

CH_2O in this region (because there is no CH_2O available). However, because NO and CH_3OO are insoluble, CH_2O is produced by the gas-phase reaction of these two species. As a result, at the upper region of the convective core, CH_2O is chemically destroyed in one simulation and produced in the other.

CH_2O chemistry in the rain drops also differs for the two simulations. Because more CH_2O resides in the rain for the simulation in which the species is retained in the frozen hydrometeor during freezing processes, aqueous reaction of CH_2O with OH is 3 times greater than that for the simulation in which the species is degassed during freezing.

5. DISCUSSION

From the analysis of sources and sinks of H_2O_2 and CH_2O given here, it appears that these soluble, reactive species are controlled by in-cloud scavenging and microphysical processes when convection is encountered. Chemical reactions appear to have a minor role, partly because the chemical sources and sinks tend to balance each other. This is likely not the case for sulfur dioxide because of its rapid chemical destruction in the cloud water and rain. When

parameterizing convection and chemical species in large-scale chemistry transport models, careful attention needs to be given to the scavenging parameterization because of its importance to the distribution of the soluble species. Further, consideration of the ice phase and its role in scavenging soluble species should be part of wet deposition parameterizations.

A comparison of the results presented here (which included aqueous-phase reactions) to results from a simulation with gas-phase chemistry only and scavenging of soluble species should be carried out. This kind of comparison will be performed next.

6. ACKNOWLEDGMENTS

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7. REFERENCES

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