HETEROGENEOUS DEGRADATION OF OXYGENATED INTERMEDIATES

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1 INTRODUCTION

Although environmental chemistry studies have tended to focus on homogeneous gas and aqueous phase processes, it has become increasingly clear over the past decade that heterogeneous mechanisms play key roles in many environmental processes among them acid deposition, formation of respirable and visibility reducing particulates, and damage to crops, vegetation, and materials. Mounting evidence also suggests that the atmospheric fates of certain chemicals, once thought to be governed by purely gas phase mechanisms, are affected by heterogeneous processes. For example, heterogeneous reactions of halogenated species on polar stratospheric clouds and sulfate aerosols can enhance stratospheric O_3 depletion. Now questions have even been raised concerning the possibility that heterogeneous reactions of oxygenated intermediates influence oxidant formation in the troposphere.

2 TROPOSPHERIC HETEROGENEOUS CHEMISTRY OF OXYGENATED INTERMEDIATES

In general, tropospheric oxygenated intermediates are formed from reactions of volatile organic compounds with OH, O_3, and NO_3. Examples of such compounds include O_3 and free radicals, carbonyl compounds, NO_x compounds, peroxides, alcohols, and organic acids. Each of these oxygenates may undergo further gas phase reactions, but each can react heterogeneously. Oxygenates can participate in nucleation processes that form new particles. They can deposit on particulates, land and vegetated surfaces, and structures. Furthermore, many of the oxygenates are water soluble and are susceptible to absorption and reaction in tropospheric aqueous media including cloudwater, fogwater, liquid precipitation, dew, hygroscopic aerosols and large aquatic bodies including lakes, rivers, streams, and oceans. Examples of oxidation products that have been detected in the troposphere are shown in Table 1. The issue that ultimately must be addressed is whether heterogeneous reactions of these types of compounds significantly affect the chemistry of the troposphere.

The uptake of gas compounds into aqueous droplets has been addressed by a number of atmospheric chemists.[1-3] The uptake of a water soluble reactive compound into an aqueous droplet of radius r and dimensionless liquid water content L has been described by the following steps: (1) transfer of the gas from the bulk gas phase to the droplet interface; (2) transfer across the gas-liquid interface; (3) volatilization of dissolved

gases; (4) dispersion of dissolved gases throughout the droplet; (5) attainment of aqueous equilibria; and (6) aqueous-phase reactions.[4]

TABLE 1 Oxygenated Intermediates

Compound Class	Examples
O_3 and Free Radicals	O_3, OH, HO_2, NO_3
Saturated Carbonyls	$HCHO$, CH_3CHO
Saturated Dicarbonyls	$CHOCHO$, CH_3COCHO
Unsaturated Carbonyls	$CH_2=CHCOCH_3$, $CH_2=CCH_3CHO$
Peroxides	$HOOH$, CH_3OOH
Organic Acids	$HCOOH$, CH_3COOH
NO_x Compounds	NO_2, N_2O_5, HNO_3, $CH_3C(O)OONO_2$

It is convenient to discuss the overall uptake process in terms of a number of time constants. τ_{mt}, the gas phase mass transfer time, is defined by

$$\tau_{mt} = r^2/3D_g + 4r/3v\alpha,$$

where $r^2/3D_g$ is the gas phase diffusion time and $4r/3v\alpha$ is the interfacial gas transfer time. D_g is the gas phase diffusion coefficient; v is the average gas phase molecular velocity; and α is the mass accommodation coefficient. Other relevant time constants include τ_{da} the aqueous phase diffusion time, τ_{ra} the aqueous phase reaction time, and τ_{rg} the gas phase reaction time. The gas-aqueous equilibrium time is defined by $\tau_{eq} = HRT\tau_{mt}$, where H is the Henrys' law constant, R is the universal gas constant, and T is the temperature.

The following system of coupled first order differential equations describes the time evolutions of the gas phase number densities n and the aqueous concentrations $[A]$

$$dn/dt = -(f_aL/\tau_{mt})(n - [A]N_{av}/HRT) + Q_g - S_g$$

and

$$d[A]/dt = (f_a/\tau_{mt})(n/N_{av} - [A]/HRT) + f_v(Q_a - S_a)$$

where N_{av} is Avogadro's number. The homogeneous chemical production rates are represented by Q_g and Q_a and the corresponding destruction rates are S_g and S_a. The constant f_v is included to take into account, perhaps in a crude way, that the aqueous media is present only some fraction of the time.

In general, a numerical solution of these equations with $f_v = 1$ and a complete parameterization of the moisture cycle is required to accurately determine the gas and aqueous phase concentrations. However, some information on how time constants affect removal of gas phase oxygenates can be obtained by solving the coupled equations for a compound that has no homogeneous gas or aqueous phase sources, but undergoes first order reactions in both phases. Assuming further that the dissolved gas concentration is at steady state, the equations for the gas and aqueous phase concentrations can be combined and rearranged to yield the following loss equation

$$dn/dt = -(1/\tau_h + 1/\tau_{rg})n,$$

where the heterogenous removal time τ_h is

$$\tau_h = \tau_c(1 + \tau_{ra}/\tau_{eq}),$$

with τ_c, the heterogeneous collision time, defined by

$$\tau_c = \tau_{mt}/f_wL.$$

The expression for τ_h takes certain limiting forms based on the relative sizes of τ_{ra} and τ_{eq}. If τ_{ra} is much greater than τ_{eq}, then $\tau_h = \tau_{ra}/f_wLHRT$. Under these conditions, the equilibration process is sufficiently rapid so that the dissolved gas remains in equilibrium with its gas phase component and the heterogeneous loss is controlled by the rate of reaction in the aqueous phase. At the other extreme, where τ_{ra} is much less than τ_{eq}, $\tau_h = \tau_c$ and the uptake is controlled by gas phase mass transfer.

A simple numerical example comparing heterogeneous removal times of hypothetical cloudwater and hygroscopic aerosols serves as a useful tool for further clarifying the processes that control the uptake of gas phase compounds to aqueous droplets. τ_h values were calculated for T = 285 °K for a cloud droplet of radius 10 μm and liquid water content of 10^{-7} that was present 5% of the time and a persistent .10 μm aerosol with a liquid water content of 10^{-11}. The gas and aqueous phase diffusion coefficients were 0.1 and 1 x 10^{-5} cm^2 s^{-1}, respectively. The Henrys' law constant was 1000 mol L^{-1} atm^{-1}. The mass accommodation coefficient was 0.1 and the gas phase molecular velocity was 2 x 10^4 cm s^{-1}.

The calculated gas phase mass transfer times for the cloud droplet and aerosol were 4.0 x 10^{-6} and 7.0 x 10^{-9} s, respectively. The equilibration time for the cloudwater was 9.4 x 10^{-2} s and the corresponding value for the aerosol was 1.6 x 10^{-4} s. As expected, the gas phase mass transfer and equilibration times were much shorter for the aerosol than for the larger cloud droplet. The effective collision times were similar; the value for the aerosol was 700 s and the cloudwater value was 800 s. Figure 1 shows the heterogeneous removal time as a function of the aqueous phase reaction time.

Under some circumstances such heterogeneous reactions may be better sinks for oxygenates than homogeneous gas phase reactions. For example, gas phase reaction times for carbonyl compounds are on the order of days. Uptake to the hypothetical cloudwater starts to compete with the loss rate corresponding to τ_{rg} = 1 day when τ_{ra} is less than about 100 s. Published modeling studies suggest that there are situations where bimolecular reactions of dissolved oxygenates in cloudwater are fast enough to satisfy this type of condition. The aqueous reaction of HCHO with OH is one such example.[4] On the other hand, for the hypothetical aerosol with the much lower water content, τ_{ra} must be less than about .10 s to begin to compete with the gas phase reaction. This may require reactions in aerosols where the dissolved gas hydrolyses very rapidly or possibly reacts with highly concentrated nonvolatile species. Such aerosols might include those that are highly acidic or alkaline or contain high levels of transition metals.
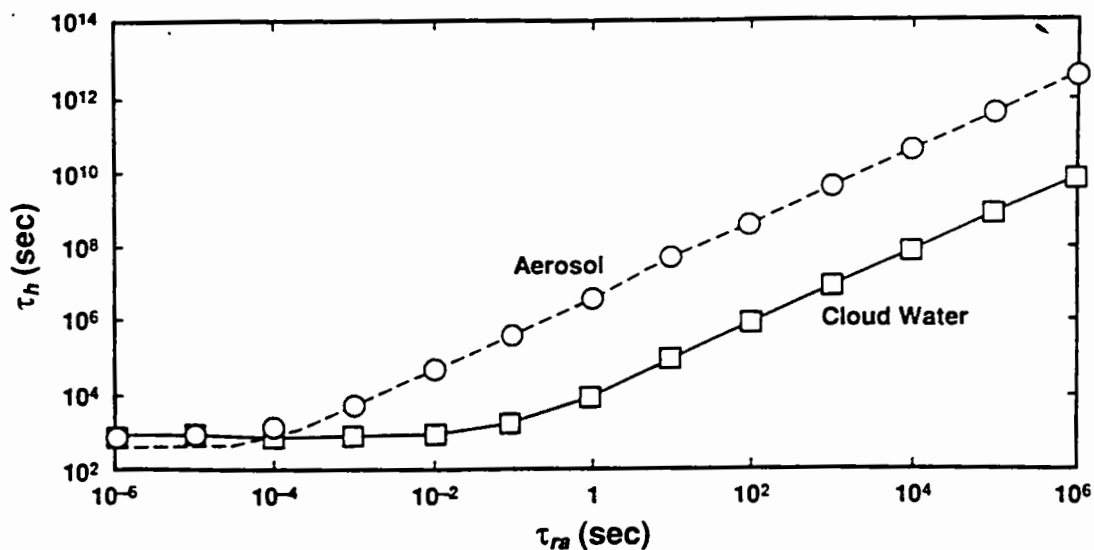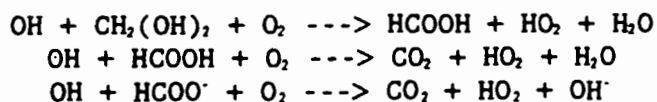
FIGURE 1 Heterogeneous removal time as a function of aqueous reaction
time

3 LITERATURE RESULTS

3.1 Effect of Cloudwater·on Global Photochemistry

Lelieveld and Crutzen conducted a modeling study to assess the impact
of cloudwater on global photochemistry.[4,5]   The global gas phase
photochemistry was based on the CH_4-CO-NO_x-HO_x system where HO_x represents
both HO_2 and OH radicals.   The aqueous reactions of the chloride,
bicarbonate, and aqueous formaldehyde, HO_x, oxidant, and hydrogen peroxide
system made up the cloudwater chemistry model.   Gas phase concentrations
were calculated for the northern and southern hemispheres and the equator,
for both winter and summer seasons.   The calculations were performed for
a single cloudwater droplet radius of 10 μm with liquid water contents
ranging from 2-4 x 10^{-7}.   A typical wetness cycle. consisted of 3 h with
clouds followed by 18 cloud free hours.   Aerosol affects were not
included.

Numerical solution of the mass balance equations showed significant
coupling between the gas. and aqueous systems, with the presence of
cloudwater decreasing HO_2, OH, HCHO, O_3, and NO_x levels.   A number of
multiphase reaction schemes that contributed to these decreases were
identified.   HCHO, HO_2, and to a far lesser extent O_3 are water soluble.
Upon dissolution in cloudwater, HCHO forms the hydrated form of HCHO,
$CH_2(OH)_2$, and HO_2 will function as a weak acid, undergoing some dissociation
forming H^+ and. the reactive species O_2^-. $CH_2(OH)_2$ reacts with aqueous OH
radicals generating HCOOH, which along with its ionization product $HCOO^-$,
can react with OH to form HO_2 and CO_2.

$$OH + CH_2(OH)_2 + O_2 \dashrightarrow HCOOH + HO_2 + H_2O$$
$$OH + HCOOH + O_2 \dashrightarrow CO_2 + HO_2 + H_2O$$
$$OH + HCOO^- + O_2 \dashrightarrow CO_2 + HO_2 + OH^-$$

This aqueous reaction scheme conserves HO_x but it is an overall HO_x sink
because it removes gas phase HCHO that otherwise could photolyze to form
two HO_2 radicals.

$$HCHO + h\nu + 2O_2 \longrightarrow 2HO_2 + CO$$

The aqueous reaction between O_3 and O_2^- is an important component of the coupling scheme because it is a sink for gas phase O_3 and in effect cycles HO_2 back to reactive OH.

$$O_3 + O_2^- + H_2O \longrightarrow OH + 2O_2 + OH^-$$
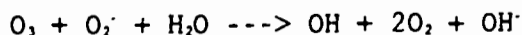
Dissolution of HO_2 also interferes with O_3 production by separating the highly soluble HO_2 radical from slightly soluble NO. This reduces the conversion of NO to NO_2 by HO_2. Irreversible absorptions of NO_3 radicals and N_2O_5 by cloudwater, important nighttime processes, remove reactive NO_x compounds from the gas phase.

The modeling results showed that the presence of cloudwater reduced NO_x, HCHO, and HO_x concentrations by 20 to 30% in the summer and 65 to 80% in the winter. On the average, for each O_3 molecule consumed by the gas phase reaction sequence

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \longrightarrow 2OH$$
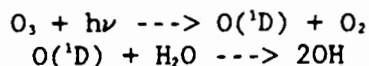
approximately 10 to 15 O_3 molecules were destroyed by aqueous reaction in the winter and 1 to 2 in the summer. The model simulations also showed that net O_3 destruction in NO_x poor regions increased by factors of 2 to 4. In NO_x rich areas net O_3 formation rates decreased about 40%.

3.2 N_2O_5 and NO_3 Reactions in Cloudwater and Tropospheric Aerosol

Dentener and Crutzen conducted a modeling study to investigate the impact of heterogeneous removal of reactive NO_x compounds by uptake to cloudwater and tropospheric aerosols on global photochemistry and springtime smog formation in the northeastern United States.[6] The global gas phase chemistry was again based on the CH_4 oxidation mechanism. Iso-butane served as the surrogate compound for biogenic and anthropogenic hydrocarbons for the smog simulations. Heterogeneous removal involving cloudwater and aerosols was limited to that due to N_2O_5 and NO_3. Gas phase mass transfer controlled uptake to aerosols and the cloudwater cycling time controlled removal by cloudwater.

The modeling results showed that cloudwater and hygroscopic aerosols decreased global NO_x concentrations by 50% and O_3 and OH concentrations by 9%. The major removal process in the northern hemisphere was uptake to hygroscopic sulfate aerosols. In the tropics and southern hemisphere, where there are lower aerosol levels, liquid cloudwater served as an additional sink. Furthermore, heterogeneous reactions may also affect traditional smog formation. Heterogeneous reactions of NO_3 and N_2O_5 on sulfate aerosols reduced springtime O_3 levels in the northeast United States by 15%. However, this O_3 reduction was not very sensitive to the aerosol concentration, but rather was controlled mainly by the reaction of NO_2 with O_3 that forms NO_3.

3.3 Sea Salt Aerosol Reactions in the Marine Boundary Layer

Chameides and Stelson investigated heterogeneous reactions in sea salt aerosols in the marine boundary layer.[7] The purpose of the study was (1) to try to explain the 3-4 neq m^{-3} of non-sea salt SO_4^{2-} found in sea salt aerosols in the marine boundary layer and (2) to assess whether chloride

deficits found in these aerosols could be due to reactions of chloride with aqueous O_3 or OH that form volatile Cl_2. The size of the Cl deficit is sufficient to produce Cl_2 levels that could alter atmospheric lifetimes of gas phase compounds.

The calculations were conducted for a constant composition clean air photochemical mixture in the presence of a distribution of alkaline sea salt aerosols. Aqueous reactions of the chloride, bromide, sulfur oxide, bicarbonate and aqueous HO_x, oxidant, and hydrogen peroxide system made up the aerosol chemistry model. Model simulations were conducted for a 1.2 μm aerosol with a liquid water content of 1.5×10^{-10} at 96% relative humidity and for a 0.75 μm aerosol with a liquid water content of 3.7×10^{-11} at 80% relative humidity. The non-ideal nature of the aerosols was taken into account by including activity coefficients.

The proposed reaction schemes did not explain the chloride deficits. Reaction of dissolved O_3 with aerosol chloride is too slow to affect the budgets of chloride or O_3. Reactions of Cl^- ions with aqueous OH can form Cl radicals. However, the Cl radicals will react with Cl^- to form Cl_2^- that then reacts mainly with O_2^- and HO_2 to form two Cl^-. The overall reaction simply conserves the chloride ion concentration. On the other hand, SO_2 oxidation by O_3 can generate about 0.75 neq m^{-3} of non-sea salt SO_4^{2-}. This removes $1-4 \times 10^{11}$ mol of SO_2 per year from the marine boundary layer, a significant quantity. The alkalinity of the aerosol accelerates the reaction between O_3 and S(IV) compounds, with the buffering capacity essentially controlling the SO_2 removal.

3.4 Transition Metal Catalyzed Reactions of HO_2 Radicals on Tropospheric Aerosols

Ross and Noone carried out a modeling study to determine if Cu catalyzed reactions of HO_2 radicals on tropospheric hygroscopic ammonium bisulfate aerosols were sufficiently fast so that under ambient conditions the heterogeneous reaction is likely to be compete with the homogeneous gas phase HO_2 recombination reaction.[8] In their analysis, the heterogeneous removal time for the Cu catalyzed reaction was compared with the reaction time for the gas phase HO_2 recombination reaction. The chemical and physical characteristics of the aerosols were based on field data from a site in central Sweden. The calculations were performed for a range of humidities.

The model calculations showed that for humidities less than 90%, the Cu concentrations exceeded .01 mol L^{-1} and the catalyzed aqueous recombination reaction was sufficiently rapid so that the uptake rate was controlled by gas phase mass transfer. Only at higher relative humidities did the aqueous rate of reaction influence r_h. Comparison of r_h with r_{rg} for the gas phase HO_2 recombination reaction showed that for an HO_2 concentration of 10 pptv removal by aerosols was faster than the gas phase reaction when the relative humidity exceeded 85%. In addition to copper, iron and manganese, transition metals commonly present in atmospheric aerosols, may catalyze removal of H_2O_2 on atmospheric aerosols. However, these metals as well as copper could be tied up in complexes that prevent their serving as effective catalysts and thus questions remain in terms of the atmospheric implications of this study.

4 LABORATORY INVESTIGATION OF HETEROGENEOUS REMOVAL OF OXYGENATED INTERMEDIATES

Recently we carried out a laboratory screening study (1) to determine the extent that oxygenated intermediates of an irradiated o-xylene/NO_x/SO_2 mixture are taken up into aqueous media and (2) to establish their fate upon evaporation of the aqueous media. Here the preliminary results of the study are presented.

4.1 Experimental

The experiment was conducted using the fully instrumented dew point controlled continuous stirred tank reactor shown in Figure 2 to irradiate o-xylene/NO_x/SO_2/air mixtures. The resulting steady state smog mixtures were exposed to aqueous films on stainless steel panels, located in an external exposure chamber that contained no lights. Each of the seven port positions in the exposure chamber was equipped with a chiller back plate to maintain panel temperatures below the air dew point, thus minimizing evaporation. The air flow through the exposure chamber was turbulent, with wind speeds of 3 m s^{-1}. At the end of the exposure, the films were collected and analyzed for their ionic and carbonyl contents. Carbonyl concentrations were determined using the 2,4 di-nitro-phenol-hydrazine method. Details concerning the operation of the reactor and exposure chamber and the gas and aqueous phase chemical analyses are reported elsewhere.'
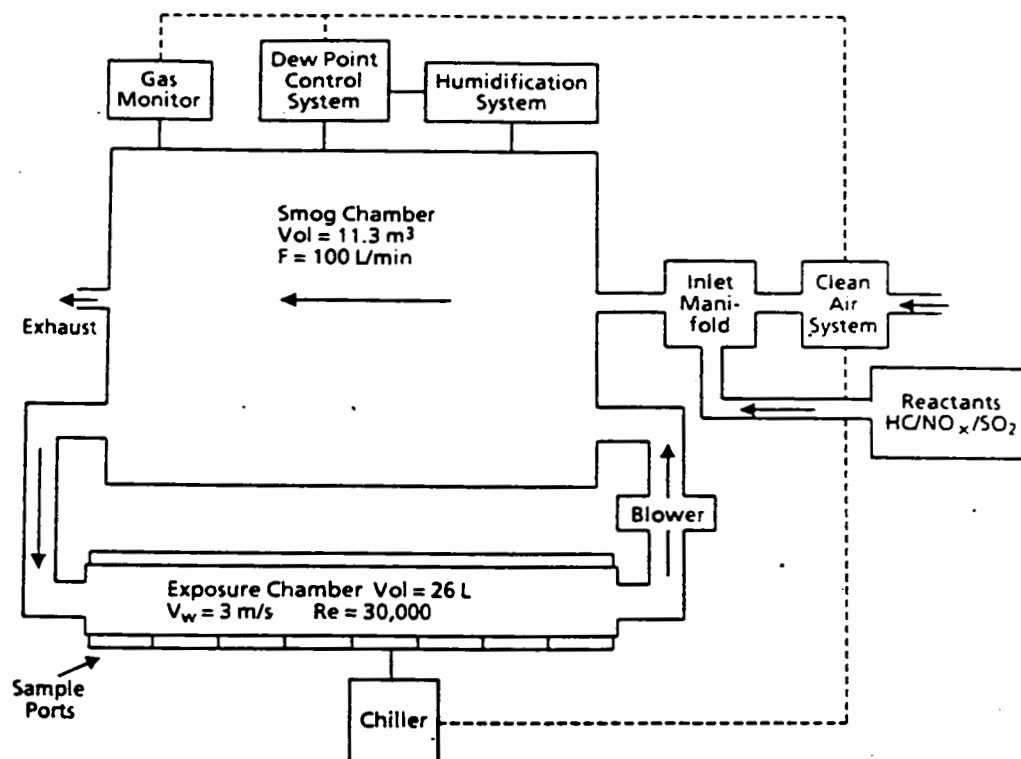

FIGURE 2 Continuous stirred tank reactor and exposure chamber

The second phase of the experiment consisted of placing one ml aliquots of exposed aqueous film samples in a Teflon tube and passing clean dry air across the aliquot to enhance evaporation. Two bubblers containing deionized (DI) water were placed in series at the end of the tube to collect volatile water soluble evaporation products. Once the aliquot

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evaporated, the tube was rinsed twice with DI water and the rinse and the contents of the bubbler were chemically analyzed.

Three separate five hour exposure experiments were conducted where aqueous films, approximately 0.5 mm in thickness, initially containing 47.2 nmol cm^{-2} of H_2O_2 were exposed to irradiated o-xylene/NO_x/SO_2/air mixtures. H_2O_2 was introduced into the films to control the SO_2 deposition. The average chemical composition of the irradiated steady state mixtures is shown in Table 2.

TABLE 2 Average Chamber Gas Concentrations

Compound	Concentration (ppb)
o-xylene	1170
NO_x	285
NO	15
HNO_3	7
O_3	31
SO_2	91
HCHO	25
CH_3CHO	4
CHOCHO	6
CH_3COCHO	57
$(CH_3CO)_2$	16
$2-CH_3C_6H_4CHO$	7
HCOOH	23
CH_3COOH	38

4.2 Results and Discussion

The ions CH_3COO^-, $HCOO^-$, NO_3^-, SO_3^{2-}, SO_4^{2-}, and H^+ were detected in the exposed acidic aqueous films. The carbonyl analysis showed the presence of HCHO, CHOCHO, and CH_3COCHO. The aqueous concentrations were converted into fluxes J that were used to calculate the effective deposition velocity v_d using the equation $J = v_d n$. The results, that are based on 21 measurements, are shown in Table 3.

TABLE 3 Effective Deposition Velocities

Compound	v_d(cm s^{-1})
SO_2	0:72 ± 0.03
HNO_3	0.88 ± 0.10
HCOOH	0.71 ± 0.11
CH_3COOH	0.41 ± 0.05
HCHO	0.33 ± 0.02
CHOCHO	2.00 ± 0.40
CH_3COCHO	0.90 ± 0.10

SO_2, HNO_3, HCOOH, CH_3COOH and the carbonyl compounds HCHO, CH_3COCHO, and CHOCHO deposited to the films. Gas phase mass transfer controlled uptake of highly soluble HNO_3. Results of previous experiments suggest that under these conditions SO_2 uptake is limited by the amount of H_2O_2 available to oxidize HSO_3^-.[9] The deposition data were not sufficient to unravel the factors controlling the uptakes of the remaining carbon bearing oxidation

products. Gas phase transfer, saturation effects, and possibly aqueous reactions could have affected the uptakes.

The evaporation results shown in Table 4 were obtained from chemical analyses of the bubbler contents and tube rinses. Another important experimental result is the observation that a residue formed during evaporation that did not dissolve in the DI rinses. The quantity in the table labelled collected is the sum of the amounts detected in the bubbler samples and tube rinses. % volatile is the percentage of this total that was found in the bubblers.

TABLE 4 Evaporation Results

Compound	Applied nmol	Collected nmol	% Volatile
CH_3COO^-	158	143	85
$HCOO^-$	111	112	80
NO_3^-	49	22	100
SO_4^{2-}	412	429	0
H^+	692	756	13
HCHO	58	46	100
CHOCHO	72	0	-
CH_3COCHO	357	63	100

Most of the CH_3COO^- and $HCOO^-$ was recovered as gas phase CH_3COOH and HCOOH. As expected, all the SO_4^{2-} was collected in the tube rinse, most of it probably as H_2SO_4. The HCHO data are consistent with significant volatilization of HCHO. There were major losses of NO_3^-, CHOCHO, and CH_3COCHO. Only 45% of the NO_3^- was recovered, all as volatile gas phase species, most likely HNO_3. No CHOCHO was detected in the tube rinses or the bubblers. Only 18% of the CH_3COCHO was accounted for, all of it in the gas phase.

These preliminary laboratory results suggest that CHOCHO and CH_3COCHO are subject to absorption into aqueous media and thus could possibly undergo aqueous reactions with OH radicals. The evaporation data suggest that HCHO, and HCOOH and CH_3COOH can volatilize out of evaporating acidic solutions. The absence of mass balances for CHOCHO, CH_3COCHO and NO_3^- and the presence of a water insoluble residue raises the interesting possibility that uptakes of these dicarbonyl compounds and HNO_3 to aqueous media are not always completely reversible and they could contribute to aerosol formation. However, the laboratory data are also consistent with the formation of volatile evaporation products that were not detected. Further investigations are required to define the fate processes and to assess whether these results have atmospheric implications.

5 CONCLUSIONS

Modeling studies suggest heterogeneous reactions of oxygenated intermediates can in principle affect the chemistry of the troposphere. There appear to be situations where reactions of dissolved oxygenated intermediates are sufficiently fast so that they can compete with homogeneous gas phase reactions and by doing so affect O_3, HCHO, free radical and NO_x concentrations. In addition, there is some evidence that highly reactive aerosols may serve as sinks for oxygenates.

However, these studies were based by and large on complex multiphase mechanisms that although representing the best available information, lack

experimental confirmation. Furthermore, field verification of the model predictions is, in general, lacking. In the case of O_3 formation, uncertainties in homogeneous gas phase mechanisms and hydrocarbon and NO_x emission inventories may mask the importance of heterogeneous processes. Thus the key question of whether heterogeneous processes significantly affect tropospheric pollution levels such as O_3 concentrations remains unanswered.

Additional modeling and laboratory studies are needed to assess the impact of heterogeneous reactions. The multiphase chemical model should include the types of processes discussed here, but also other important processes including the adsorption and absorption of low volatility oxidation products, inorganic aerosol chemistry, and photo-induced radical production in aqueous media.[10] Laboratory studies should be conducted (1) to measure uptake coefficients of oxygenated intermediates as functions of the chemical composition of the aqueous media and the photolytic condition; (2) to refute or confirm multiphase reaction schemes; (3) to further refine the underpinnings of the chemistry of low volatility oxidation products; and (4) to investigate reactions in aerosols and in evaporating media.

6 REFERENCES

1. Schwartz, S.E. in NATO, Adv. Sci. Ser. (ed. Jaeschke, W.), Vol. G6, 415-471, 1986.
2. Chameides, W.L. J. Geophys. Res., 89, 4739-4755, 1984.
3. Jacob, D.J. J. Geophys. Res., 91, 9807-9826, 1986.
4. Lelieveld, J. and P.J. Crutzen. J. Atmos. Chem., 12, 229-267, 1991.
5. Lelieveld, J. and P.J. Crutzen. Nature, 343, 227-233, 1990.
6. Dentener, F.J and P.J. Crutzen. J. Geophys. Res., 98, 7149-7163, 1993.
7. Chameides, W.L. and A.W. Stelson. J. Geophys. Res., 97, 20565-20580, 1992.
8. Ross, H.B. and K.J. Noone. J. Atmos. Chem., 12, 121-136, 1991.
9. Edney, E.O. D.J. Driscoll, E.W. Corse, and F.T. Blanchard. Atmos. Environ., 28, 1189-1196, 1994.
10. Faust, B.C. and J.M. Allen. J. Geophys. Res., 97, 12913-12926, 1992.

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16. ABSTRACT

Issues surrounding the importance of including heterogeneous processes when determining the fate of oxygenated intermediates in the troposphere are discussed. Results of recent investigations are reviewed and preliminary data from a laboratory study are presented. In the laboratory study heterogeneous processes that determine the fate of oxidation products of irradiated o-xylene/NOX/SO2/air mixtures were investigated. The review includes summaries of (1) the effect of oxidant reactions in cloud water on global photochemistry; (2) the impact of N2O5 and NO3 reactions in cloud water on global photochemistry; (3) the effect of sea salt aerosol reactions in cloud water and tropospheric aerosols; and (4) the impact of transition metal catalyzed reactions of HO2 radicals on tropospheric aerosols.

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