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Secondary organic aerosol formation from cyclohexene ozonolysis in the presence of water vapor and dissolved salts

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ABSTRACT

A series of 90 experiments were conducted in the UC Riverside/CE-CERT environmental chamber to evaluate the impact of water vapor and dissolved salts on secondary organic aerosol formation for cyclohexene ozonolysis. Water vapor (low – 30 ± 2% RH, medium – 46 ± 2% RH, high – 63 ± 2% RH) was found to directly participate in the atmospheric chemistry altering the composition of the condensing species, thus increasing total organic aerosol formation by ~22% as compared to the system under dry (<0.1% RH) conditions. Hygroscopicity measurements also indicate that the organic aerosol composition is altered in the presence of gaseous water. These results are consistent with water vapor reacting with the crigee intermediate in the gas phase resulting in increased aldehyde formation. The addition of dissolved salts ($(NH_4)_2SO_4$, NH_4HSO_4, $CaCl_2$, NaCl) had minimal effect; only the $(NH_4)_2SO_4$ and NaCl were found to significantly impact the system with ~10% increase in total organic aerosol formation. These results indicate that the organics may be partitioning to an outer organic shell as opposed to into the aqueous salt. Hygroscopicity measurements indicate that the addition of salts does not alter the aerosol composition for the dry or water vapor system.

1. Introduction

Secondary organic aerosol (SOA) are particles formed in the atmosphere from the oxidation of parent hydrocarbons. These particles may impact human morbidity and mortality, visibility, and the earth's radiation budget (Eldering and Cass, 1996; Pilinis et al., 1995; Schwartz et al., 1996). There is a large discrepancy between measurement and model predictions of atmospheric SOA concentrations (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). SOA formation is commonly estimated from environmental chamber studies that oxidize a single parent hydrocarbon and report the amount of SOA formed. These experiments are conducted under a variety of conditions including different water vapor concentrations and in the presence of dry and dissolved inorganic salts.

Atmospheric relative humidity (RH) can vary widely; however, it is common for environmental chamber experiments to operate under dry conditions, loosely defined as <10% relative humidity (RH). While some environmental chambers have conducted experiments under higher values of RH (>60%), few have explicitly explored the impact of increased levels of RH on SOA formation. The presence of a dissolved salt in fine particulate matter is also commonly found in the atmosphere. These salts can be formed from aerosolizing sea water or can be chemically formed from gaseous pollutants (e.g., HNO_3 and ammonia to form ammonium nitrate).

Pankow (1994a,b) and Odum et al. (1996) developed a semi-empirical thermodynamic approach to describe SOA formation. The gas to particle partitioning coefficient ($K_{om,i}$) describes semi-volatiles condensing into and out of the particle phase. $K_{om,i}$ for an individual compound is

$$K_{om,i} = \frac{RT}{MW_{om,i}\gamma_i p^o_{L,i}} \tag{1}$$

where R is the ideal gas constant, T is temperature, $MW_{om,i}$ is the molecular weight of the organic compound i, γ_ι is the activity coefficient of compound i, and $p^o_{L,i}$ is the saturation liquid vapor pressure of compound i. Therefore, $K_{om,i}$ depends on environmental conditions and the thermodynamic properties of the particles formed. SOA formation described as the fractional aerosol yield (Y) is dependent on the final organic mass of aerosol (M_o) and is expressed as

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$$Y = \sum_i Y_i = M_o \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \tag{2}$$

where α_i is the mass based stoichiometric coefficient of compound *i*.

Water vapor can participate in gas phase chemical reactions (Atkinson, 1990; Becker et al., 1993), altering α_i from the dry SOA formation system. For example, Na et al. (2006) reported that the presence of water vapor alters gas phase chemistry for styrene ozonolysis resulting in a reduction of low vapor pressure products, and thus reducing SOA formation. Similarly, Na et al. (2007) reported that water vapor reduces SOA formation from α-pinene ozonolysis, likely due to gas phase reactions, while Cocker et al. (2001a) reported that water vapor had no impact on its SOA formation. Additionally, the presence of water may impact the partitioning capabilities of semi-volatiles in the system. For example, polar compounds produced from the oxidation of hydrocarbons may more readily absorb into water, increasing the $K_{om,i}$ relative to the dry system. Also, the general increase in particle mass, from water absorption, may promote organic partitioning based on the yield expression. Water within a particle may alter the γ_i of the subsequent organic compounds, also impacting $K_{om,i}$. Water may also participate in particle phase reactions, directly and indirectly, by partaking in reactions or causing an increase or decrease of organic mass within the particles that do undergo particle phase reactions.

In addition to water vapor, the presence of dissolved inorganic salts may affect SOA formation by altering the γ_i in the particle, changing $K_{om,i}$. Cocker et al. (2001a) reported a decreasing trend in aerosol formation for α-pinene ozonolysis with the addition of $CaCl_2$, NH_4HSO_4, and $(NH_4)_2SO_4$, respectively. Iinuma et al. (2004) observed that gas absorption is increased in an acidic seed, thus increasing SOA formation. A thermodynamic model, presented by Chang and Pankow (2006), predicted that both the addition of water vapor and dissolved salts can effect SOA formation positively and negatively depending on the predicted products from parent hydrocarbon oxidation and the properties of the ionic solution.

Cyclohexene ozonolysis was chosen for further investigation of water vapor and dissolved salts' effect on SOA formation because of its relative simplicity, previous experimentation conducted under dry conditions, available product speciation, and theorized SOA formation mechanism (Kalberer et al., 2000). In addition, previous hygroscopicity measurements have been conducted on aerosol generated from cyclohexene ozonolysis by Varutbangkul et al. (2006).

2. Experimental description

The experiments for this study were conducted in the UC Riverside/CE-CERT environmental chamber, which has been fully described elsewhere (Carter et al., 2005). Briefly, the environmental chamber consists of a temperature-controlled enclosure that is continually flushed with purified air. Within the enclosure, two 90 m^3 Teflon (2 mil FEP Teflon) film reactors are suspended on a rigid frame that descends during the experiment to maintain a slight positive differential pressure between the reactors and the enclosure. Hydrocarbons are introduced into the reactors by injecting a known liquid (high purity) volume into a glass manifold and flushed into the reactors in a pure N_2 stream. Ozone is injected into the reactors using two ozone generators supplied with 20 psi of purified air. Carbon monoxide (CO) is directly injected from a CO cylinder (99.9% purity). CO is used as the hydroxyl scavenger, with sufficiently high concentrations injected to react with >99% of the hydroxyl radicals produced. Particle-free water vapor is injected using a two-unit system. Unit one contains distilled water with submerged heaters to maintain a desired water temperature, which determines the water vapor concentration in the air stream, while unit two contains a 1 μm filter. Purified air is bubbled through the water and then passes through the filter before entering the reactors.

Hydrocarbon concentrations are monitored using Agilent 5890 and 6890 gas phase chromatographs equipped with flame ionization detection. A Dasibi Environmental Corp. 1003-AH Ozone analyzer, Thermal Environmental Instruments model 40C CO analyzer, and a Thermal Environmental Instruments model 42C chemiluminescent NO_x analyzer monitored ozone (O_3), CO, and

Table 1
Experimental conditions and results for cyclohexene ozonolysis at four RH conditions (high (H) – 63 ± 2%, medium (M) – 46 ± 2%, low (L) – 30 ± 2%, dry (D) – <0.1%).

Exp number	RH[a]	O_3 (initial) [ppb]	ΔCyclohexene [μg m^{-3}]	$M_{org+water}$ [μg m^{-3}]	M_{org} [μg m^{-3}][b]
460A	D	196	300	25	25
460B	D	214	300	27	27
462A	D	224	170	11	11
463A	D	110	97	2.5	2.5
463B	D	142	57	1.0	1.0
530A	D	280	383	37	37
530B	D	362	98	6.5	6.5
532A	D	273	257	21	21
535A	D	195	534	42	42
535B	D	215	354	27	27
596A	D	175	314	20	20
596B	D	293	317	20	20
638A	D	312	430	44	44
638B	D	401	224	22	22
639A	D	352	107	6.0	6.0
639B	D	230	647	60	60
654A	D	347	410	38	38
654B	D	390	407	32	32
$655A^T$	D	364	434	34	34
$657A^T$	D	431	400	33	33
657B	D	487	400	30	30
$668A^T$	D	349	297	28	28
668B	D	378	300	23	23
464A	L	188	154	15	14
464B	L	267	477	55	51
466A	L	210	103	6.7	6.2
466B	L	244	53	2.6	2.4
553A	L	378	285	37	34
577A	L	393	174	21	19
577B	L	333	177	16	15
605A	L	134	307	37	34
605B	L	367	310	35	32
611B	L	289	302	35	32
627B	L	476	400	56	52
$646A^T$	L	380	390	42	38
646B	L	336	390	42	39
$667A^T$	M	370	409	57	47
465B	M	588	174	15	12
667B	M	373	414	52	43
465A	M	213	444	54	45
623B	M	310	541	80	66
542A	H	288	85	12	7.5
576B	H	346	174	25	16
635B	H	357	227	33	21
459B	H	250	290	43	27
459A	H	230	297	44	28
609B	H	162	316	47	30
542B	H	243	321	49	31
610B	H	265	324	49	31
608B	H	194	333	53	34
608A	H	263	344	55	35
633B	H	333	604	112	71

T in superscript represents TDMA hygroscopicity measurements taken.

[a] D – <0.1% RH, L – 30 ± 2% RH, M – 46 ± 2% RH, H – 63 ± 2% RH.

[b] The aerosols water component was removed (WR) using experimental hygroscopicity measurements ($G_{f,org}$ – Fig. 3) (Eq. (6)).