A General Theoretical Method for Evaluating the Formation of High-Molecular Weight/Low-Volatility Compounds and Their Contribution to Atmospheric Organic Particulate Matter

Kelley Claire Barsanti

B.A., Biology and Environmental Science, University of Colorado, 1996M.S., Environmental Science and Engineering, Oregon Graduate Institute, 2001

A dissertation presented to the faculty of the OGI School of Science & Engineering at Oregon Health & Science University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Science and Engineering

March 2006

The dissertation "A General Theoretical Method for Evaluating the Formation of High-Molecular Weight/Low-Volatility Compounds and Their Contribution to Atmospheric Organic Particulate Matter" by Kelley Claire Barsanti has been examined and approved by the following Examination Committee:

> Dr. James Pankow Professor Dissertation Research Advisor

Dr. James Huntzicker Department Head Department of Management in Science & Technology

> Dr. Eladio Knipping Senior Technical Manager-Air Quality Electric Power Research Institute

Dr. James Schauer Associate Professor University of Wisconsin-Madison

ACKNOWLEDGEMENTS

This dissertation would not have been possible without the tremendous guidance and support from so many people. First and foremost, I would like to acknowledge my advisor, Dr. James Pankow. Thank you for the extraordinary amount of time you spend with each of your students, and in my case, the extraordinary amount of patience that went along with it. Thank you for helping me turn my interest in environmental science into passion. Finally, I thank you for the exciting opportunities that now await me, which would not exist without your excellent mentorship.

I would like to acknowledge the additional members of my defense committee: Dr. James Huntzicker, Dr. Eladio Knipping, and Dr. James Schauer, I thank each of you for your continued support of my research and for taking the time to serve on my committee, asking thoughtful questions and providing valuable feedback.

I would like to acknowledge and thank members of the Pankow group: Bill Asher, for your online journal access and for your ever-amusing emails; Lorne Isabelle and Wentai Lou, for your help with my smoking experiments and for bringing your laughter to our group meetings; Elsa Chang, for your company as a fellow traveler at many meetings and for our numerous discussions on work, life, and "other"; Cai Chen, for your company as a fellow student and for motivating me to finish my dissertation; Garnet Erdakos, for your friendship and for inspiring many young women (including me) to pursue careers in science; Ameer Tavakoli for your bizarre sense of humor and for fielding innumerable questions regarding my research.

I would also like to acknowledge and thank many others that have made my experiences at OGI truly memorable: Patty Toccalino and Paul Tratnyek, for your open doors and words of wisdom; Nancy Christie, Terrie Hadfield, Jim Mohan, and the Grad Ed and Library staff, for "life" support in general; Sergey Frolov, Ryan Kilgren, and Philip Orton for all the bike rides and occasional commiseration (Iavor Diatchki too, for the latter); Esther Klabbers and Rudolph van der Merwe for blazing a trail; and my fellow students and the EBS faculty and staff, for creating a positive learning environment.

I would like to acknowledge my friends outside of OGI: Michelle DeChesser, thank you for your endless encouragement and your infinite wisdom (especially when it comes to fashion and food); Jen Alfieri, thank you for providing a refuge (especially in the early days); Sarah Hohne, thank you for your life-long friendship; Kathryn Bonuck, Valerie Chandler, Anna Dennis, Beth Parazette, Heidi Scheiblehner, thank you for your fabulous senses of humor and all of the shared laughter; to each of you and AOC, I thank you for providing balance in my life and helping me explore the world outside of OGI.

Finally, I would like to acknowledge my family, without whom I never could have made this journey: My mother and father, Pam and Ron, and my brother, Cameron, I thank you for your constant support and encouragement, even when you weren't sure what it was that I was doing; Brad, I thank you for your patience and for believing in me, even when I didn't...or wasn't convinced. I love you all very much and dedicate this work to you.

TABLE OF CONTENTS

Approval Page	
Acknowledgements	iii
Table of Contents	V
List of Tables	ix
List of Figures	xi
Notation	xiii
Abstract	xviii
CHAPTER 1 Introduction	1
1.1. General Background	1
1.2. Overview	2
1.3. Theory	4
1.4. Cases	5
1.5. Format of Dissertation	6
1.6. References	7
CHAPTER 2 Thermodynamics of the Formation of Atmospheric Organic Particulate Matter by Accretion Reactions: Aldehydes and Ketones	10
2.1. Introduction	10
2.2. Theory	12
2.2.1. Free energy of reaction (ΔG°) and equilibrium constant (<i>K</i>)	12
2.2.2. A criterion for the importance of OPM formation by an accretion reaction (Π)	14

2.3. Mathe	ematical Solution Process	15
2.3.1.	Estimation of free energies of formation $(\Delta G_{\rm f}^{\rm o})$	15
2.3.2.	Estimation of vapor pressures $(p_{\rm L}^{\rm o})$	15
2.3.3.	Extent of reaction at equilibrium (ɛ)	20
2.4. Cases		22
2.5. Result	ts and Discussion	25
2.5.1.	Predicted OPM formation for <i>n</i> -aldehydes; $A_0 \approx 10,000 \ \mu \text{g m}^{-3}$ and $n_{\text{na}} = 0$	25
2.5.2.	Predicted $\triangle OPM$ formation for <i>n</i> -aldehydes; $A_0 \approx 10,000 \ \mu g \ m^{-3}$ and $n_{na} \neq 0$	27
2.5.3.	Predicted OPM formation by pinonaldehyde and pinonaldehyde- like compounds at varying A_0 ; $n_{na} \neq 0$	29
2.6. Refere	ences	30
Particulate and Diketo	Matter by Accretion Reactions: Dialdehydes, Methylglyoxal, ones	33
3.1. Introd		دد رد
3.2. Theor	y	30
2.2.1	Estimation of up an approximate (2) and free energies of formation	43
3.3.1.	Estimation of vapor pressures (p_L) and free energies of formation (ΔG_c°)	43
3.3.2.	Mass balance	45
3.4. Cases		46
3.5. Result	ts and Discussion	46
3.5.1.	Predicted OPM formation; $A_0 = 10^{-3}$ to $10^4 \ \mu g \ m^{-3}$ and $RH = 20\%$.	46
3.5.2.	Predicted OPM formation; $A_0 = 10 \ \mu g \ m^{-3}$ and $RH = 10 \ to \ 90\% \ \dots$	51
3.5.3.	Uncertainties in $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ values: implications for predicted OPM formation	51
3.6. Refere	ences	55

CHAPTER 4 Particulate	Thermodynamics of the Formation of Atmospheric Organic e Matter by Accretion Reactions: Carboxylic and Dicarboxylic	
Acids		58
4.1. Introc	luction	58
4.2. Theor	ry	61
4.3. Mathe	ematical Solution Process	62
4.3.1.	Estimation of vapor pressures $(p_{\rm L}^{\rm o})$ and free energies of formation $(\Delta G_{\rm f}^{\rm o})$	62
4.3.2.	Mass Balance	62
4.4. Cases	5	64
4.5. Resul	ts and Discussion	64
4.5.1.	Predicted OPM formation in Case 1; $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$, MBO ₀ and DEA ₀ = 1 $\mu g \ m^{-3}$, NH ₃ = 0.07 $\mu g \ m^{-3}$, and RH = 20%	64
4.5.2.	Predicted OPM formation in Case 2; $A_0 = 1 \ \mu g \ m^{-3}$, MBO ₀ and DEA ₀ = 1 $\mu g \ m^{-3}$, NH ₃ = 0.07 $\mu g \ m^{-3}$, and RH = 5% to 95%	71
4.5.3.	Implications for observed oligomer formation in chamber studies	74
4.6. Refer	ences	79
CHAPTER 5 Particulate	Thermodynamics of the Formation of Atmospheric Organic e Matter by Accretion Reactions: General Theoretical Framework	82
5.1. Introd	luction	82
5.2. Mathe	ematical Solution Process	84
5.2.1.	Mass Balance	84
5.2.2.	Estimation of vapor pressures (p_{i}°) and free energies of formation	
	$(\Delta G_{\rm f}^{\rm o})$	84
5.3. Cases	3	85
5.4. Resul	ts and Discussion	85
5.4.1.	Predicted OPM formation as a function of log K and p_r° ;	
	$A_0 = 10 \ \mu g \ m^{-3}$, $OPM_{na} = 10 \ \mu g \ m^{-3}$, and $RH = 50\%$	85
5.4.2.	Evaluating the potential contribution of individual accretion reactions atmospheric OPM	s to 90
5.5. Refer	ences	100

CHAPTER 6	Conclusions	102
6.1. Resul	ts Summary	102
6.1.1.	OPM formation by accretion reactions of aldehydes and ketones	102
6.1.2.	OPM formation by accretion reactions of dialdehydes and diketones	103
6.1.3.	OPM formation by accretion reactions of carboxylic and dicarboxylic acids	103
6.1.4.	OPM formation by general accretion reactions	104
6.2. Implie	cations for Organic Aerosol Modeling	104
6.3. Refer	ences	106
APPENDIX 1		107
APPENDIX 2		110
BIOGRAPHI	CAL SKETCH	113

LIST OF TABLES

Table 2.1	Reported and estimated $\Delta G_{\rm f}^{\rm o}$ values, and estimated $p_{\rm L}^{\rm o}$ values for	
	water, 1-decanol, and parent <i>n</i> -aldehydes	16
Table 2.2	Estimated $\Delta G_{\rm f}^{\rm o}$ and $p_{\rm L}^{\rm o}$ values for accretion products of interest	17
Table 2.3	Initial and equilibrium amounts of each of the reactants and products in Equations (2.1) and (2.2) expressed in terms of ε (extent of reaction) values	21
Table 2.4	Initial concentrations of <i>n</i> -aldehydes (A_0) , 1-decanol (B_0) , H ₂ O, and OPM _{na} for the five case types considered	24
Table 3.1	Major types of accretion products and their formation reactions, types of linkages, and relevance for organic particulate matter (OPM) formation in the atmosphere	37
Table 3.2	Summary of reactants and accretion products of potential interest	41
Table 3.3	Summary of accretion products, types, and linkages	42
Table 3.4	Molecular groups with $\Delta H_{\rm f}^{\rm o}$ and $S^{\rm o}$ data unavailable in the CHETAH (2002) database and their interpolated $\Delta H_{\rm f}^{\rm o}$ and $S^{\rm o}$ values (dialdehyde and diketone groups)	44
Table 3.5	Predicted additional OPM levels ($\mu g m^{-3}$) for "base case" and three additional cases	53
Table 4.1	Molecular groups with $\Delta H_{\rm f}^{\rm o}$ and <i>S</i> ^o data unavailable in the CHETAH (2002) database and their interpolated $\Delta H_{\rm f}^{\rm o}$ and <i>S</i> ^o values (carboxylic and dicarboxylic acid groups)	63
Table 4.2	Summary of accretion reactions and products of interest, including type of product and linkage	66

Table 4.3	Summary of accretion products, including type and linkage, for accretion reactions of pinic acid with hydrated ring products of hydroxy pinonaldehyde and pinonaldehyde
Table 4.4	Predicted total additional OPM by esterification of pinic acid and hydrated ring-opening products of hydroxy pinonaldehyde and pinonaldehyde
Table 5.1	Reported and estimated p_1° and ΔG_{f}° values for water, NH ₃ , pinic
	acid, and three general accretion products; and calculated ΔG° and K values for accretion product formation from pinic acid
Table A1.1	Definitions of parameters used in data extractions from Jang and Kamens (2001)
Table A1.2	Data extracted from selected chamber experiments of Jang and Kamens (2001)
Table A2.1	Estimated log <i>K</i> values and accretion product/parent carbonyl ratio for hydrate and hemiacetal formation in liquid solution
Table A2.2	Estimated log <i>K</i> values and accretion product/parent carbonyl ratio for acetal formation in liquid solution at equilibrium, and for α,β - unsaturated carbonyl formation in liquid solution at equilibrium112

LIST OF FIGURES

Figure 2.1	Potential accretion reactions of interest for atmospheric aldehydes and ketones: a. hydrate, hemiacetal, acetal, and oligomer formation; b. aldol condensation
Figure 2.2	Measured $\triangle OPM$ versus predicted $\triangle OPM$
Figure 3.1	Accretion products of potential interest for glyoxal
Figure 3.2	Accretion product of potential interest for 1,4-butanedial40
Figure 3.3	Predicted total additional OPM for each dicarbonyl reactant as a function of initial dicarbonyl concentration
Figure 3.4	Dominant accretion products of glyoxal for $A_0 = 10^{-3}$ to 10^4 49
Figure 3.5	Dominant accretion products of methylglyoxal $A_0 = 10^{-3}$ to 10^4
Figure 3.6	Predicted total additional OPM for each dicarbonyl reactant as a function of relative humidity (RH)
Figure 4.1	Parent carboxylic and dicarboxylic acids
Figure 4.2	Accretion reactions of interest for acetic, malic, maleic, and pinic acids
Figure 4.3	Predicted total additional OPM by accretion reactions of acetic, malic, maleic, and pinic acids as a function of A_0
Figure 4.4	Fractional contribution of each of the dominant accretion products to total additional OPM as a function of A_0 (maleic acid)
Figure 4.5	Fractional contribution of each of the dominant accretion products to total additional OPM as a function of A_0 (malic acid)
Figure 4.6	Fractional contribution of each of the dominant accretion products to total additional OPM as a function of A_0 (pinic acid)70

Figure 4.7	Predicted levels of total additional OPM as a function of NH ₃ concentration	72
Figure 4.8	Potential ring-opening schemes and products of hydroxy pinonaldehyde and pinonaldehyde	75
Figure 5.1	Predicted additional OPM formation as a function of log <i>K</i> and $p'_{\rm LC}$ (2A = C, butanal)	86
Figure 5.2	Predicted additional OPM formation as a function of log <i>K</i> and $p'_{\rm LC}$ (2A = C, hexanal)	87
Figure 5.3	Predicted additional OPM formation as a function of log <i>K</i> and $p'_{\rm LC}$ (2A = C + H ₂ O, butanal)	88
Figure 5.4	Predicted additional OPM formation as a function of log <i>K</i> and p_{LC}° (2A = C + H ₂ O, hexanal)	89
Figure 5.5	Predicted OPM formation by C as a function of log K and $p_{L,C}^{\circ}$ (A + NH ₃ = C + H ₂ O, butanal)	91
Figure 5.6	Predicted OPM formation by C as a function of log K and $p_{L,C}^{\circ}$ (A + NH ₃ = C + H ₂ O, hexanal)	92
Figure 5.7	Predicted OPM formation by C as a function of log K and $p_{I,C}^{\circ}$ (A + NH ₃ = C + H ₂ O, pinic acid)	93
Figure 5.8	Predicted OPM formation by C as a function of log K and $p_{I,C}^{\circ}$ (A + B = C + H ₂ O, pinic acid)	94
Figure 5.9	Predicted OPM formation by C as a function of log K and $p_{I,C}^{\circ}$ (A + 2B = C + 2H ₂ O, pinic acid)	95
Figure 5.10	Amide and ester formation from pinic acid	97

NOTATION

$A_g(\mu g m^{-3})$	atmospheric constituent A in the gas phase (also, concentration of atmospheric constituent A in the gas phase)
$\mathbf{A}_{\mathrm{liq}}$	atmospheric constituent A in the liquid-like particle phase
$A_0 (\mu { m g}~{ m m}^{-3})$	initial concentration of reactant A
$B_g(\mu g m^{-3})$	atmospheric constituent B in the gas phase (also, concentration of atmospheric constituent B in the gas phase)
B _{liq}	atmospheric constituent B in the liquid-like particle phase
$B_0 (\mu { m g}~{ m m}^{-3})$	initial concentration of reactant B
$C_g(\mu g m^{-3})$	accretion product C in the gas phase (also, concentration of accretion product C in the gas phase)
$C_{liq}(\mu g m^{-3})$	accretion product C in the liquid-like particle phase (also, concentration of accretion product C in the particle phase)
$C_{C,g}(\mu g m^{-3})$	gas-phase concentration of accretion product C
$C_{\rm C,liq}$ (µg m ⁻³)	particle-phase concentration of accretion product C
$c_{\rm g,C} ({\rm ng \ m^{-3}})$	gas-phase concentration of accretion product C
$c_{\mathrm{p,C}}(\mathrm{ng}\ \mathrm{\mu g}^{-1})$	particle-phase concentration of accretion product C
СНЕТАН	computer program for CHEmical Thermodynamics And energy release evaluation (Δ H)
$DEA_0 (\mu g m^{-3})$	initial concentration of diethylamine
$f_{ m p}$	fraction of a compound in the particle phase
$\Delta_{\mathrm{G},j}(\mathrm{kJ} \mathrm{mol}^{-1})$	Gibbs free energy of formation for a group <i>j</i> , where <i>j</i> is a functional or structural group

ΔG° (kJ mol ⁻¹)	standard Gibbs free energy of reaction
$\Delta G_{\rm f}^{\rm o}$ (kJ mol ⁻¹)	molar Gibbs free energy of formation for a compound in the standard state of an ideal gas at 1 atm and temperature $T(K)$
G/P	gas/particle
$\Delta H_{\rm f}^{\rm o}$ (kJ mol ⁻¹)	standard enthalpy of formation
$\Delta HC (\mu g m^{-3})$	amount of reacted hydrocarbon
HULIS	humic-like substances
Κ	equilibrium constant
Kacetal	equilibrium constant for acetal formation
K _c	equilibrium constant for condensation
Khemiacetal	equilibrium constant for hemiacetal formation
K _{hydrate}	equilibrium constant for hydrate formation
$K_{lpha,eta}$ -unsaturated carbonyl	equilibrium constant for α,β -unsaturated carbonyl formation
$K_{\beta-hydroxycarbonyl}$	equilibrium constant for β -hydroxycarbonyl formation
$K_{\rm p}$ (m ³ µg)	absorptive gas/particle partitioning constant
$MBO_0 (\mu g m^{-3})$	initial concentration of 2-methyl-3-buten-1,2-ol
$MW (g mol^{-1})$	molecular weight
MW_C (g mol ⁻¹)	molecular weight of accretion product C
MW_{OM} (g mol ⁻¹)	mean molecular weight of the absorbing phase
MW_{OPM} (g mol ⁻¹)	mean molecular weight of the absorbing phase
MW_{na} (g mol ⁻¹)	mean molecular weight of the absorbing phase not related to accretion reactions
$n_{\rm B}$ (mols)	number of mols of reactant B
n_i (mols)	number of mols of compound <i>i</i>

$n_{\rm na}$ (mols)	number of mols in condensed phase not related to accretion reactions
$n_{\rm OPM}$ (mols)	number of mols in condensed phase related to accretion reactions
$n_{\rm A,0}$ (mols)	initial number of mols of reactant A
$n_{\mathrm{B},0} \ \mathrm{(mols)}$	initial number of mols of reactant B
$n_{\mathrm{C},0}$ (mols)	initial number of mols of accretion product C (usually = 0)
$n_{i,0}$ (mols)	initial number of mols of compound <i>i</i>
$n_{i,g}$ (mols)	equilibrium number of mols of compound <i>i</i> in the gas phase
$n_{i,\mathrm{liq}}$ (mols)	equilibrium number of mols of compound <i>i</i> in the liquid-like particle phase
$n_{i,g,0}$ (mols)	initial number of mols of compound i in the gas phase
Δn_i (mols)	change in the number of mols of compound i , relative to the initial number of mols of compound i
$\Delta n_{i,\text{gas}}$ (mols)	change in the number of mols of compound i in the gas phase, relative to the initial number of mols of compound i in the gas phase
$\Delta n_{i,\text{liq}} \text{ (mols)}$	change in the number of mols of compound i in the particle phase, relative to the initial number of mols of compound i in the particle phase
Ν	number of possible accretion products from reactant A
Nj	number of groups of type j , where j is a functional or structural group
NM	non-methane
NMVOCs	non-methane volatile organic compounds
OPM (µg m ⁻³)	organic particulate matter
<i>p</i> (atm)	partial pressure
$p_{\rm A}$ (atm)	equilibrium partial pressure of reactant A

$p_{\rm B}$ (atm)	equilibrium partial pressure of reactant B
$p_{\rm C}$ (atm)	equilibrium partial pressure of accretion product C
p_i (atm)	partial pressure of compound <i>i</i>
$p_{\rm L}^{\rm o}$ (atm)	pure-liquid vapor pressure
$p_{\mathrm{A},0}$ (atm)	initial partial pressure of reactant A
$p_{\mathrm{B},0}$ (atm)	initial partial pressure of reactant B
P (atm)	atmospheric pressure
PAHs	polycyclic aromatic hydrocarbons
PM ($\mu g m^{-3}$)	particulate matter
predicted ΔOPM	(total OPM predicted to form in the presence of the initial n_{na} value) – (OPM corresponding to the initial n_{na})
reported ∆OPM	(OPM reported with acidic-seed aerosol)-(OPM reported with non-
R (kJ mol ⁻¹ K ⁻¹ ; m ³ atm mol ⁻¹ K ⁻¹)	ideal gas constant
RH (%)	relative humidity
S° (J mol ⁻¹ K ⁻¹)	standard entropy
SPARC	Sparc Performs Automated Reasoning in Chemistry
<i>T</i> (K)	temperature
TPM ($\mu g m^{-3}$)	total particulate matter
UNIFAC	UNIQUAC (UNIversal QUAsi-Chemical) Functional Activity Coefficients
$v_{\rm OPM} ({\rm nm}^3{\rm cm}^{-3})$	volume concentration of OPM
$v_{\text{seed}} (\text{nm}^3 \text{cm}^{-3})$	seed volume concentration
$v_{\rm TPM} ({\rm nm}^3{\rm cm}^{-3})$	total PM volume concentration
$V(m^3)$	volume

$V(\text{uL m}^{-3})$	injected liquid organic volume				
VOCs	volatile organic compounds				
Xacetal	mole fraction of acetal in solution				
Xalcohol	mole fraction of parent alcohol in solution				
X _{carbonyl}	mole fraction of parent carbonyl in solution				
Xhemiacetal	mole fraction of hemiacetal in solution				
X _{hydrate}	mole fraction of hydrate in solution				
X_i	mole fraction of compound i in the condensed phase				
$X_{ m unsaturated\ carbonyl}$	mole fraction of unsaturated carbonyl in solution				
X _{water}	mole fraction of water in solution				
X _C	mole fraction of accretion product C in the condensed phase				
Greek Symbols					

3	extent of reaction at equilibrium
ε _a	extent of accretion product formation at equilibrium
ε _c	extent of condensation at equilibrium
€ _{a,j}	extent of accretion product formation, for accretion reaction j , at equilibrium
€c,j	extent of condensation, for accretion product from accretion reaction j , at equilibrium
Vi	stoichiometric coefficient for compound <i>i</i>
$ u_{i,j}$	stoichiometric coefficient for compound i in accretion reaction j (carries sign)
Ω	saturation index for vaporization of a multi-component liquid mixture
Π (μg m ⁻³)	criterion for the importance of OPM formation by an accretion reaction

$\Pi_{\alpha,\beta}$ -unsaturated carbonyl ($\mu g m^{-3}$)	criterion for the importance of OPM formation by an aldol condensation product, α , β -unsaturated carbonyl
$\Pi_{C} (\mu g \ m^{-3})$	criterion for the importance of OPM formation by accretion product C
Σ_j	summation over multiple (<i>j</i> number of) accretion reactions
Σ_k	summation over multiple (k number of) aldehyde or ketones
ζ_i	activity coefficient of compound <i>i</i> in the absorbing phase on a mole fraction scale
ζc	activity coefficient of accretion product C in the absorbing phase on a mole fraction scale

ABSTRACT

A General Theoretical Approach for Evaluating the Formation of High-Molecular Weight/Low-Volatility Compounds and Their Contribution to Atmospheric Organic Particulate Matter

Kelley Claire Barsanti

Ph.D., OGI School of Science & Engineering at Oregon Health & Science University March 2006

Research Advisor: Dr. James F. Pankow

Predicting the formation of organic particulate matter (OPM) in the atmosphere by absorptive gas/particle (G/P) partitioning requires a knowledge of the identities, atmospheric levels, and physical properties of all condensable species. It is known that a portion of atmospheric OPM samples are comprised of products generated during oxidation of volatile organic compounds. Additionally, initially formed oxidation products may undergo reactions with one another and/or other atmospheric constituents, i.e. "accretion reactions", leading to the formation of high-molecular weight (MW)/lowvolatility compounds that can form OPM. The proposed mechanism by which oxidation products and other atmospheric constituents (e.g., A and B) may contribute to OPM formation is: $A_g + B_g = C_g$ (accretion), then $C_g \leftrightarrow C_{liq}$ (condensation). Initially, chamber studies focused on accretion reactions as a general mechanism for OPM formation and the potential role of acid-catalysis in increasing OPM formation by this mechanism; more recently, such studies have focused on detection and quantification of accretion products and on the effects of particle acidity and parent compound structure on accretion product formation. However, many uncertainties exist regarding accretion reactions as they may occur in the atmosphere, including identification of specific accretion products and their formation pathways.

A general theoretical method has been developed to evaluate thermodynamic favorabilities of accretion reactions, including the extent to which they may contribute to atmospheric OPM. If an accretion reaction is to produce significant OPM, appreciable amounts of the product C must form, and the vapor pressure of C must be relatively low so that a significant proportion of C can condense into the multi-component liquid OPM phase. In considerations of aldehydes, ketones, dialdehydes, methylglyoxal, diketones, carboxylic and dicarboxylic acids, it was concluded that: 1) the types of accretion reactions considered are not favorable for mono- and diketones and $\sim C_5$ and lower mono- and dialdehydes; 2) aldol condensation of $\sim C_6$ and higher mono- and dialdehydes may contribute to atmospheric OPM formation under some circumstances; 3) diol and diolologiomer formation from glyoxal, aldol condensation of methylglyoxal, and esterification and amide formation from carboxylic and dicarboxylic acids are thermodynamically favorable, and may contribute significantly to OPM in the atmosphere.

CHAPTER 1

Introduction

1.1 General Background

Scientific interest in atmospheric aerosols began in the late 1700's. Since that time, particulate matter (PM) in the atmosphere has been linked to a number of adverse effects including visibility degradation, transport of toxic compounds to remote locations, global climate change, and compromised respiratory function in humans (Jacobson et al., 2000). The extents of such effects are influenced by the concentration and composition of PM in the atmosphere. PM can be emitted directly into the atmosphere (primary) or formed in-situ (secondary). Most atmospheric aerosols are comprised of both primary and secondary PM; the major constituents of which are nitrates, sulfates, ammonium, elemental carbon, and numerous organic compounds. While the inorganic fractions are relatively well characterized, the organic fraction remains poorly understood, though it often comprises a significant fraction of total aerosol mass (Seinfeld and Pankow, 2003).

Understanding the chemical composition of organic PM (OPM) formed in the atmosphere remains one of the significant challenges to accurately representing organic aerosols in regional and global air quality and climate models (Kanakidou et al., 2005). Efforts to identify and quantify the numerous constituents found in atmospheric OPM samples have met with marginal success: molecular level characterizations usually account for only 10-20% of the total OPM mass (e.g., Rogge et al., 1993; Mazurek, 2002). While chemical and physical complexity alone cause a large portion of the problem of identifying and quantifying the numerous constituents present in atmospheric

OPM samples, another portion is likely related to the presence of difficult to determine, high-molecular weight (MW)/low-volatility compounds.

Data from field and chamber experiments have shown that oxidation of volatile organic compounds (VOCs) leads to the formation of multi-functional products, some of which condense to form OPM. Additionally, it has been suggested that such products may undergo reactions with one another and/or other atmospheric constituents, i.e. "accretion reactions", leading to the formation of high-MW/low-volatility compounds that can easily condense, thereby contributing to atmospheric OPM. Studies have shown that a significant fraction of atmospheric OPM may be comprised of high-MW compounds* (e.g., Havers et al., 1998; Samburova et al., 2005), which would be consistent with the occurrence of such accretion reactions in the atmosphere (e.g., Jang et al., 2002). However, many uncertainties exist regarding accretion reactions as they occur in the atmosphere, including identification of those reactions most likely to contribute to OPM formation and the potential significance of OPM formation by this mechanism.

1.2 Overview

Existing evidence supports the view that PM formation in the atmosphere can be modeled based on absorptive gas/particle (G/P) partitioning theory, wherein the tendencies of oxidation products (and other compounds) to condense are largely controlled by their pure-liquid vapor pressures, $p_{\rm L}^{\circ}$ (Pankow 1994a,b; Pankow et al., 2001).

*Such high-MW compounds have also been referred to as HULIS (humic-like substances, Havers et al., 1998), macromolecules (Zappoli et al., 1999), and "oligomers" (Tolocka et al., 2003). There is no specific upper size cutoff for usage of the term "oligomer". Nevertheless, "oligomer" has generally been used to refer to a polymer which is large enough that removing one or two units will not greatly change the physical properties of the molecule. By this definition, an oligomer is a polymer in which the number *n* of repeating monomer units is ~10, so that one repeating unit contributes ~10% of the mass of the overall oligomer molecule. Ultimately, as *n* becomes rather "large", the term "polymer" is usually used.

The equilibrium mass fraction of a compound that is in the particle phase is given by (Pankow, 1994a)

$$f_{\rm p} = K_{\rm p} \text{TPM} / (1 + K_{\rm p} \text{TPM}) \tag{1.1}$$

where K_p (m³ µg⁻¹) is the absorptive G/P partitioning constant and TPM (µg m⁻³) is the total concentration of particulate matter into which a compound can condense (= OPM neglecting water and inorganic compounds). Even for TPM levels as large as 100 µg m⁻³, in order for $f_p \ge 0.1$ (i.e., $\ge 10\%$ in the particle phase), $K_p \ge 10^{-3}$ µg m⁻³. Absorptive G/P partitioning theory (Pankow, 1994a) then predicts that for significant condensation to occur, $p_L^o \le 10^{-7}$ atm.

It has been suggested by Jang and Kamens (2001b) and Tobias and Ziemann (2000) that some oxidation products with $p_{\rm L}^{\rm o}$ values in the range 10^{-8} to 10^{-4} atm may have a role in the formation of OPM. The proposed mechanism by which such compounds (e.g., A and B) may contribute to OPM formation is

$$A_g + B_g \leftrightarrow C_g$$
 accretion in the gas phase, then (1.2)

$$C_g \leftrightarrow C_{liq}$$
 condensation of the accretion product (1.3)

in which C is a higher-MW/lower-volatility compound that can further condense into the PM phase. In general, for compounds within a given compound class, vapor pressures decrease by approximately half an order of magnitude for every carbon added, so that dimerization of a compound with a carbon number of 10 can be expected to lead to a product that is roughly $\sim 10^{-5}$ times less volatile than the parent compound. The hypothesis that such reactions can occur reversibly has been advanced as an explanation for the measurement of anomalously-large, apparent K_p values for some relatively volatile organic oxidation products (Kamens and Jaoui, 2001). In particular, it has been proposed that PM-phase accretion products can revert, during chemical analysis of OPM samples to the volatile parent compounds, giving the appearance of anomalously-high PM-phase concentrations for the parent compounds (Jang and Kamens, 2001a).

Since a wide variety of different types of reactions and cross reactions can occur among compounds A, B, etc., Barsanti and Pankow (2004) introduced the term "accretion reactions" to refer to the large collection of reactions by which atmospheric organic constituents can add mass, especially as by combination with other organic compounds. Simple oxidation reactions were excluded from this definition. Chamber studies initially focused on accretion reactions as a general mechanism for atmospheric OPM formation (e.g., Jang and Kamens, 2001b); and more recently on the affects of aerosol seed properties (e.g., particle acidity) and parent compound structure on OPM formation (Gao et al., 2004a,b; Kalberer et al., 2004; Tolocka et al., 2004). However, many uncertainties still exist regarding accretion reactions as they may occur in the atmosphere. For example, specific accretion reactions have not been confirmed and some of the proposed reactions are not thermodynamically feasible (Barsanti and Pankow, 2004, 2005). Thus the objectives of the research presented herein were to: 1) develop a general theoretical method to evaluate the thermodynamic favorabilities of accretion reactions, including the extent to which they may contribute to OPM formation in the atmosphere; and 2) apply that method to evaluate OPM formation by accretion reactions of several classes of compounds representative of organic oxidation products in the atmosphere.

1.3 Theory

The net reaction represented by Equations (1.2) and (1.3), $A_g + B_g \leftrightarrow C_{liq}$, is well suited for thermodynamic analysis. Equilibrium for an accretion reaction (e.g., as shown in Equation (1.2)) is governed by the equilibrium constant *K* (expressed here in terms of partial pressures *p* (atm))

$$K = \frac{p_{\rm C}}{p_{\rm A} p_{\rm B}} \tag{1.4}$$

Analogous expressions of Equation (1.4) exist for reaction stoichiometries different from that shown in Equation (1.2), such as 2A = C or $A + B = C + H_2O$. For any accretion reaction, *K* is set by the standard Gibbs free energy of reaction (ΔG°) according to

$$\Delta G^{\circ} = \sum_{i} v_{i} \Delta G_{\rm f}^{\circ} = -RT \ln K \qquad (1.5)$$

where $\Delta G_{\rm f}^{\circ}$ (kJ mol⁻¹) is the molar Gibbs free energy of formation of *i* in the standardstate of an ideal gas at 1 atm and temperature *T* (K), and *R* (8.314 x 10⁻³ kJ mol⁻¹ K⁻¹) is the ideal gas constant. Condensation of an accretion product (e.g., as shown in Equation (1.3)) is governed largely its $p_{\rm L}^{\rm o}$ value and is set by its $K_{\rm p}$ value according to (Pankow 1994a,b)

$$K_{\rm p} = \frac{C_{\rm c,liq} \times \text{OPM}}{C_{\rm c,g}} = \frac{RT}{10^6 \,\text{MW}_{\rm OM} \zeta_i p_{\rm L,i}^\circ}$$
(1.6)

where $C_{c,liq}$ and $C_{c,g}$ (µg m⁻³) are the OPM- and gas-phase concentrations of C, OPM (µg m⁻³) is the total concentration of organic particulate matter into which C can condense, R (8.2 x 10⁻⁵ m³ atm mol⁻¹ K⁻¹) is the ideal gas constant, MW_{OM} (g mol⁻¹) is the mean molecular weight of the absorbing phase, and ζ_i is the activity coefficient of *i* in the absorbing phase on a mole fraction scale.

The overall thermodynamic tendency for an accretion reaction to form additional OPM is a product of four factors: 1) the portion of the driving force for accretion that is provided by the initial gas-phase pressures of the reactants (i.e., by $p_{A,0}$ and $p_{B,0}$); 2) the *K* for the accretion reaction as it is set by the corresponding ΔG° ; 3) the tendency of C to condense as determined by the p_L° -dependent G/P partitioning equation for K_p (Pankow, 1994a); and 4) the concentration of OPM into which the accretion product can condense. Thus, if an accretion reaction between two atmospheric constituents is to produce significant additional OPM, appreciable amounts of the product C must form, and the vapor pressure of C must be relatively low so that a significant proportion of that C can condense into the multi-component liquid OPM phase.

1.4 Cases

In order to evaluate OPM formation by accretion reactions of atmospherically relevant constituents, several classes of compounds were considered, including aldehydes, ketones, and carboxylic acids. Specific accretion reactions of aldehydes and ketones (Chapter 2), and dialdehydes and diketones (Chapter 3), included hydration, oligomerization, hemiacetal/acetal formation, and aldol condensation; specific accretion reactions of carboxylic and dicarboxylic acids (Chapter 4) included ester and amide formation. Initial concentrations of reactants and other parameters such as background OPM levels, temperature, and relative humidity were chosen to best represent ambient conditions, or where applicable, experimental conditions.

1.5 Format of Dissertation

This dissertation contains reproductions of three individual manuscripts that have been accepted for publication (permission to reproduce manuscripts granted by Elsevier) and one manuscript suitable for publication. For each of those chapters, the corresponding manuscripts are given below.

Chapter Number	Corresponding Manuscript		
2	Barsanti and Pankow, 2004		
3	Barsanti and Pankow, 2005		
4	Barsanti and Pankow, 2006		
5	Barsanti and Pankow, in preparation		

1.6 References

- Barsanti, K.B., Pankow, J.F., 2004. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 1: Aldehydes and ketones. *Atmospheric Environment* 38, 4371-4382.
- Barsanti, K.B., Pankow, J.F., 2005. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 2: Dialdehydes, methylglyoxal, and diketones. *Atmospheric Environment* 39, 6597-6607.
- Barsanti, K.B., Pankow, J.F., 2006. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 3: Carboxylic and dicarboxylic acids. *Atmospheric Environment*, submitted.
- Gao, S., Keywood, M., Ng, N.L., Surratt, J., Varutbangkul, R.B., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004a. Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α-pinene. *Journal of Physical Chemistry A* 108, 10147-10164.
- Gao, S., Ng, N.L., Keywood, M., Varutbangkul, R.B., Bahreini, R., Nenes, A., He, J., Yoo, K.Y., Beauchamp, J.L., Hodyss, R.P., Flagan, R.C, Seinfeld, J.H., 2004b. Particle phase acidity and oligomer formation in secondary organic aerosol. *Environmental Science and Technology* 38, 6582-6589.
- Havers, N., Burpa, P., Lambert, J., Klockow, D., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *Journal of Atmospheric Chemistry* 29, 45-54.
- Jacobson, M.C., Hansson, H.C., Noone, K.J., and Charlson, R.J., 2000. Organic atmospheric aerosols: review and state of the science. *Reviews of Geophysics* 38, 267-294.
- Jang, M., Kamens, R.M., 2001a. Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environmental Science and Technology* 35, 3626-3639.
- Jang, M., Kamens, R.M., 2001b. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology* 35, 4758-4766.
- Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* 298, 814-817.

- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U., 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* 12, 1659-1662.
- Kamens, R.M., Jaoui, M., 2001. Modeling aerosol formation from α -pinene + NO_x in the presence of natural sunlight using gas-phase kinetics and gas-particle partitioning theory. *Environmental Science and Technology* 35, 1394-1405.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modeling: a review. *Atmospheric Chemistry and Physics* 5, 1053-1123.
- Mazurek, M.A., 2002. Molecular identification of organic compounds in atmospheric complex mixtures and relationship to atmospheric chemistry and sources. *Environmental Health Perspectives* 110, 995-1003.
- Pankow, J.F., 1994a. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185-188.
- Pankow, J.F., 1994b. An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* 28, 189-193.
- Pankow, J.F., Seinfeld, J.H., Asher, W.E., Erdakos, G.B., 2001. Modeling the formation of secondary organic aerosol. 1. Application of theoretical principles to measurements obtained in the α -pinene-, β -pinene-, sabinene-, Δ^3 -carene-, and cyclohexene-ozone systems. *Environmental Science and Technology* 35, 1164-1172.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., 1993. Quantification of organic aerosols at a molecular level: identification, abundance and seasonal variability. *Atmospheric Environment* 27a, 1309-1330.
- Seinfeld, J.H., Pankow, J.F., 2003. Organic atmospheric particulate material. *Annual Review of Physical Chemistry* 54, 121-140.
- Samburova, V., Kalberer, M., Zenobi, R., 2005. Characterization of high molecular weight compounds in urban atmospheric particles. *Atmospheric Chemistry and Physics Discussions* 5, 437-454.

- Tobias, H.J., Ziemann, P.J., 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environmental Science and Technology* 34, 2105-2115.
- Tolocka, M.P., Jang, M., Ginter, J.M., Cox, F.J., Kamens, R.M., Johnston, M.V., 2004. Formation of oligomers in secondary organic aerosol. *Environmental Science and Technology* 38, 1428-1434.
- Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, Á., Mészáros, E., Hansson, H.C., Rosman, K., Zebühr., Y., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmospheric Environment* 33, 2733-2743.

CHAPTER 2

Thermodynamics of the Formation of Atmospheric Organic Particulate Matter by Accretion Reactions: Aldehydes and Ketones

2.1 Introduction

The formation of organic particulate matter (OPM) in the atmosphere frequently occurs as a consequence of the oxidation of volatile organic compounds (VOCs). Available evidence supports the view that the formation and evaporation of such atmospheric OPM can be predicted based on absorptive gas/particle (G/P) partitioning theory (Pankow, 1994a,b; Pankow et al., 2001; Seinfeld et al., 2001). This approach requires a knowledge of the identities, atmospheric levels, and physical properties of all condensable species, and indicates that significant condensation of a compound is not likely to occur unless its liquid vapor pressure (p_L^{o}) is less than about 10⁻⁷ atm. This criterion is based on the fact that the equilibrium mass fraction of a compound that is in the PM phase is given by $f_p = K_p TPM/(1 + K_p TPM)$ where $K_p (m^3 \mu g^{-1})$ is the overall G/P partitioning constant and TPM ($\mu g m^{-3}$) is the total concentration of particulate matter into which a compound can condense (Pankow, 1994b). Thus, even for TPM levels as large as 100 $\mu g m^{-3}$, in order for $f_p \ge 0.1$ (10% in the particle phase), then $K_p \ge 10^{-3} m^3$

It has been suggested by Tobias and Ziemann (2000) and Jang and Kamens (2001a,b) that some constituents with $p_{\rm L}^{\rm o}$ values in the range 10⁻⁸ to 10⁻⁴ atm may combine to form new compounds that can condense to form OPM. The term "accretion reaction" is therefore introduced to refer to the large collection of reactions by which

atmospheric organic constituents can add mass, especially as by combination with other organic compounds. (Reactions with oxygen that are purely oxidative in nature are not included in the accretion reaction category.) Most accretion reactions will lead to a reduction in volatility in the parent compounds so that condensation to form atmospheric OPM becomes more extensive. One kinetic scheme according to which two compounds (e.g., A and B) may thereby contribute to OPM formation is

> Scheme I: $A_g + B_g = C_g$ accretion in the gas phase, then (2.1) $C_g = C_{lig}$ condensation of the accretion product (2.2)

in which C is a relatively low vapor pressure product that can condense in significant amounts into the multi-component liquid PM phase. (In general, for compounds within a given compound class, $p_{\rm L}^{\rm o}$ values decrease by approximately half an order of magnitude for every carbon added, so that dimerization of a compound with a carbon number of 10 will lead to a product that is only ~10⁻⁵ as volatile as the parent compound.) Two other kinetic schemes are possible:

Scheme II:

$$B_g = B_{liq}$$
 condensation of B, then (2.3)

$$A_g + B_{liq} = C_{liq}$$
 accretion on the particle surface (2.4)

Scheme III:

 $A_g + B_g = A_{liq} + B_{liq}$ condensation of A and B, then (2.5)

$$A_{liq} + B_{liq} = C_{liq}$$
 accretion in the PM phase (2.6)

The net overall reaction for all three schemes is

$$A_g + B_g = C_{liq} \tag{2.7}$$

The thermodynamic tendency remains the same regardless of the actual predominating kinetic scheme by which reaction (2.7) occurs. Therefore, the conclusions of thermodynamic analysis for such an overall gas/particle system will not, in general, depend on how the accretion reaction occurs, or on whether a relevant catalyst is present in the PM phase. (Implicit in the latter point is the assumption that the catalyst does not significantly alter the thermodynamic stability of the partitioning species in the PM

phase; matters related to effects of the composition of the PM phase are discussed further in Section 2.5.2.)

For aldehydes and ketones, common organic oxidation products in the atmosphere, the accretion reactions that have been proposed (see Figure. 2.1) include hydration, oligomerization, hemiacetal/acetal formation, and aldol condensation (Jang et al., 2002; Tobias and Ziemann, 2000). Moreover, the hypothesis that such reactions can occur reversibly has been advanced as an explanation for the measurement of anomalously-large, apparent K_p values for some relatively volatile organic oxidation products (Kamens and Jaoui, 2001). In particular, it has been proposed that PM-phase accretion products can revert, during chemical analysis of the PM, to the volatile parent compounds giving the appearance of anomalously high PM-phase concentrations for the parent compounds (Jang and Kamens, 2001a).

The net reaction represented by Equation (2.7) is well-suited for thermodynamic analysis. In this work, a general theoretical approach is developed based on Scheme I that can be used to evaluate the thermodynamic favorabilities of relevant accretion reactions, including the extent to which they may contribute to OPM formation in the atmosphere; that approach is used in consideration of the potential importance of the Figure 2.1 accretion reactions for aldehydes and ketones.

2.2 Theory

2.2.1 Free energy of reaction (ΔG°) and equilibrium constant (K)

The standard Gibbs free energy of any reaction (ΔG°) is related to the equilibrium constant (*K*) for that reaction according to the fundamental equation

$$\Delta G^{\circ} = \sum_{i} \nu_{i} \Delta G^{\circ}_{\mathbf{f},i} = -RT \ln K$$
(2.8)

where v_i is the stoichiometric coefficient for compound i, ΔG_f° (kJ mol⁻¹) is the standard Gibbs free energy of formation for compound i; R (8.314 x 10⁻³ kJ mol⁻¹ K⁻¹) is the ideal gas constant; and T (K) is temperature. Each v_i carries sign.



Figure 2.1 Potential accretion reactions of interest for atmospheric aldehydes and ketones: **a**. hydrate, hemiacetal, acetal, and oligomer formation; **b**. aldol condensation.

2.2.2 A criterion for the importance of OPM formation by an accretion reaction (Π)

For the accretion reaction represented in Equation (2.1), the overall thermodynamic tendency for OPM to form is a product of four factors: 1) the portion of the driving force for the accretion reaction that is provided by the initial gas-phase pressures of the reactants (i.e., by $p_{A,0}$ and $p_{B,0}$); 2) the *K* for the accretion reaction as is set by the corresponding ΔG° ; 3) the tendency of C to condense as set by ΔG° for the condensation reaction, and utilized in the problem at hand by means of the p_{L}° -dependent G/P partitioning equation for $K_{\rm p}$ (Pankow, 1994a); and 4) the concentration of extant OPM, referred to here as "OPM_{na}", into which the accretion product can condense. The subscript "na" refers to "non-accretion-related" so that OPM_{na} represents the amount of OPM formed by mechanisms other than accretion. In any real environmental situation, OPM_{na} will always be non-zero. For reaction (2.7), we therefore define Π as the following product of four groups:

$$\Pi_{\rm C} \left(\mu g \ {\rm m}^{-3}\right) = \left(p_{\rm A,0} p_{\rm B,0}\right) \times K \left[\frac{10^6 \,{\rm MW}_{\rm C}}{RT}\right] \times K_{\rm p} \times {\rm OPM}_{\rm na}$$
(2.9)

where MW_C (g mol⁻¹) is the molecular weight of the product C. Accretion reactions that occur according to other stoichiometries (e.g., A + B = C + H₂O) will have analogous definitions of Π . The factor [10⁶MW_C/*RT*] in Equation (2.9) provides all of the unit conversions required between p_C (atm) and $c_{g,C}$ (ng m⁻³), and between $c_{p,C}$ (ng µg⁻¹) and the PM-phase concentration of C (µg µg⁻¹). Whether a given accretion reaction is important in a given circumstance will be case dependent. (If the importance criterion for the overall reaction (2.7) is set at \geq 10 µg m⁻³ of additional OPM, it would be necessary that $\Pi_C > 10 \mu g$ m⁻³ since after achievement of equilibrium, then $p_A p_B < p_{A,0} p_{B,0.}$) For the aldol condensation reaction wherein two aldehyde molecules combine to form C, we have A = B, $p_{A,0} = p_{B,0}$, and $p_A = p_B$.

2.3 Mathematical Solution Process

2.3.1 Estimation of free energies of formation (ΔG_{f}^{o})

Values of $\Delta G_{\rm f}^{\circ}$ for reactants and products in the gas phase were either obtained from Yaws (1999), or if necessary, estimated using the group contribution "Joback Method" given by Reid et al. (1987) for T = 298 K as

$$\Delta G_{\rm f}^{\circ} = 53.88 + \sum_{j} N_{j} \Delta_{{\rm G},j}$$
(2.10)

where for compound *i* the parameter N_j is the number of groups of type *j*, and $\Delta_{G,j}$ is the free energy (kJ mol⁻¹) of group *j* (see Tables 2.1 and 2.2). Reid et al. (1987) report that this method predicts ΔG_f° values to within ±10 kJ mol⁻¹ for a range of different compound classes. (The utilized values from Yaws (1999) for the alcohol, aldehyde, and ketone reactants of interest here were found to agree with those predicted by the Joback method to within ±3 kJ mol⁻¹ (Table 2.1).)

2.3.2 Estimation of vapor pressures $(p_{\rm L}^{\circ})$

For the alcohol and parent aldehydes of interest, with the exception of pinonaldehyde, $p_{\rm L}^{\circ}$ values were estimated using a five-parameter Antoine parameterization with coefficients from Yaws (1999). Since Antoine coefficients were not available for pinonaldehyde, nor for any of the accretion products of interest, the $p_{\rm L}^{\circ}$ values for those compounds were estimated using the structure-based group contribution method SPARC (Hilal et al., 1994) as implemented with an online calculator (http://imblc2.chem.uga.edu/sparc/style/welcome.cfm). For water, $p_{\rm L}^{\circ}$ was calculated using a three-parameter Antoine parameterization with coefficients from Bridgeman and Aldrich (1964).

Compound	Molecular Formula	Reported $\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹) ^a	Estimated $\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹) ^b	Estimated Log $p_{\rm L}^{\circ}$ (atm)
water	H ₂ O	-228.6	†	-1.51 °
1-decanol	$C_{10}H_{22}O$	-105.6	-103.5	-4.96 ^a
formaldehyde	CH ₂ O	-102.5	<u>_</u> †	0.71 ^a
acetaldehyde	C_2H_4O	-133.0	-133.6	0.07 ^a
acetone	C_3H_6O	-152.7	-154.5	-0.52 ^a
<i>n</i> -butanal	C_4H_8O	-114.8	-116.7	-0.84 ^a
<i>n</i> -hexanal	$C_6H_{12}O$	-100.1	-99.9	-1.83 ^a
<i>n</i> -octanal	$C_8H_{16}O$	-83.3	-83.0	-2.81 ^a
<i>n</i> -decanal	$C_{10}H_{20}O$	-66.5	-66.2	-3.87 ^a
pinonaldehyde	$C_{10}H_{16}O_2$	_	-167.4	-4.55 ^d

Table 2.1 Reported and estimated $\Delta G_{\rm f}^{\circ}$ values, and estimated $p_{\rm L}^{\circ}$ values for water, 1-decanol, and parent *n*-aldehydes; P = 1 atm and T = 298 K.

^a Yaws (1999)
^b Joback method (Reid et al., 1987)
^c Bridgeman and Aldrich (1964)
^d SPARC group contribution method (Hilal et al., 1994)
[†]The Joback method as described by Reid et al. (1987) lacks sufficient groups to adequately describe the molecular structures of water and formaldehyde.
and 1 270 K.					
Parent Carbonyl	Molecular Formula of Product	Estimated $\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹) ^a	Estimated Log $p_{\rm L}^{\circ}$ (atm) ^b		
hydrates					
formaldehyde	CH_4O_2	-316.1	-5.35		
acetaldehyde	$C_2H_6O_2$	-310.1	-4.05		
acetone	$C_3H_8O_2$	-296.4	-3.51		
<i>n</i> -butanal	$C_4H_{10}O_2$	-293.3	-4.58		
<i>n</i> -hexanal	$C_6H_{14}O_2$	-276.4	-5.43		
<i>n</i> -octanal	$C_8H_{18}O_2$	-259.6	-6.39		
<i>n</i> -decanal	$C_{10}H_{22}O_2$	-242.8	-7.39		
pinonaldehyde	$C_{10}H_{18}O_3$	-343.9	-9.38		
	dim	ers			
<i>n</i> -butanal	$C_8H_{18}O_3$	-367.0	-6.22		
<i>n</i> -hexanal	$C_{12}H_{26}O_3$	-333.4	-8.09		
<i>n</i> -octanal	$C_{16}H_{34}O_{3}$	-299.7	-10.08		
<i>n</i> -decanal	$C_{20}H_{42}O_3$	-266.0	-12.10		
pinonaldehyde	$C_{20}H_{34}O_5$	-468.4	-14.64		
trimers					
<i>n</i> -butanal	$C_{12}H_{26}O_4$	-440.8	-8.11		
<i>n</i> -hexanal	$C_{18}H_{38}O_4$	-390.3	-10.98		
<i>n</i> -octanal	$C_{24}H_{50}O_4$	-339.8	-13.97		
<i>n</i> -decanal	$C_{30}H_{62}O_4$	-289.2	-17.01		
pinonaldehyde	$C_{30}H_{50}O_7$	-592.8	-20.78		
oligomers					
<i>n</i> -butanal	$C_{40}H_{82}O_{11}$	-957.12	-19.82		
<i>n</i> -hexanal	$C_{60}H_{122}O_{11}$	-788.72	-29.28		
<i>n</i> -octanal	$C_{80}H_{162}O_{11}$	-620.32	-38.68		
<i>n</i> -decanal	C ₁₀₀ H ₂₀₂ O ₁₁	-451.92	-47.73		

Table 2.2 Estimated $\Delta G_{\rm f}^{\circ}$ and $p_{\rm L}^{\circ}$ values for accretion products of interest; P = 1 atm and T = 298 K.

Parent Carbonyl	Molecular Formula of Product	Estimated $\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹) ^a	Estimated Log $p_{\rm L}^{\circ}$ (atm) ^b		
hemiacetals					
formaldehyde	$C_{11}H_{24}O_2$	-200.1	-6.87		
acetaldehyde	$C_{12}H_{26}O_2$	-194.1	-6.40		
acetone	$C_{13}H_{28}O_2$	-180.4	-6.25		
<i>n</i> -butanal	$C_{14}H_{30}O_2$	-177.3	-7.06		
<i>n</i> -hexanal	$C_{16}H_{34}O_2$	-160.4	-8.04		
<i>n</i> -octanal	$C_{18}H_{38}O_2$	-143.6	-9.06		
<i>n</i> -decanal	$C_{30}H_{62}O_2$	-126.7	-10.08		
pinonaldehyde	$C_{20}H_{38}O_3$	-227.9	-11.02		
	aceta	ls			
formaldehyde	$C_{21}H_{44}O_2$	-84.1	-7.96		
acetaldehyde	$C_{22}H_{46}O_2$	-78.1	-9.47		
acetone	$C_{23}H_{48}O_2$	-64.4	-9.60		
<i>n</i> -butanal	$C_{24}H_{50}O_2$	-61.2	-10.38		
<i>n</i> -hexanal	$C_{26}H_{54}O_2$	-44.4	-11.42		
<i>n</i> -octanal	$C_{28}H_{58}O_2$	-27.6	-12.45		
<i>n</i> -decanal	$C_{30}H_{62}O_2$	-10.7	-13.48		
pinonaldehyde	$C_{30}H_{58}O_3$	-111.9	-13.85		

Table 2.2 cont. Estimated $\Delta G_{\rm f}^{\circ}$ and $p_{\rm L}^{\circ}$ values for accretion products of interest; P = 1 atm and T = 298 K.

Parent Carbonyl	Molecular Formula of Product	Estimated $\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹) ^a	Estimated Log $p_{\rm L}^{\circ}$ (atm) ^b
	β-hydroxyc	arbonyls	
formaldehyde	$C_2H_4O_2$	-270.4	-4.08
acetaldehyde	$C_4H_8O_2$	-256.0	-3.81
acetone	$C_6H_{12}O_2$	-263.3	-3.86
<i>n</i> -butanal	$C_8H_{16}O_2$	-224.7	-4.42
<i>n</i> -hexanal	$C_{12}H_{24}O_2$	-191.1	-6.28
<i>n</i> -octanal	$C_{16}H_{32}O_2$	-157.4	-8.21
<i>n</i> -decanal	$C_{20}H_{40}O_2$	-123.7	-10.20
pinonaldehyde	$C_{20}H_{32}O_4$	-326.1	-12.28
	α,β -unsaturate	d carbonyls	
formaldehyde	C_2H_2O	-56.5	-0.20
acetaldehyde	C_4H_6O	-36.5	-0.84
acetone	$C_6H_{10}O$	-57.6	-1.76
<i>n</i> -butanal	$C_8H_{14}O$	-11.4	-2.50
<i>n</i> -hexanal	$C_{12}H_{22}O$	22.3	-4.44
<i>n</i> -octanal	$C_{16}H_{30}O$	56.0	-6.44
<i>n</i> -decanal	$C_{20}H_{38}O$	89.7	-8.48
pinonaldehyde	$C_{20}H_{30}O_{3}$	-112.7	-9.77

Table 2.2 cont. Estimated $\Delta G_{\rm f}^{\circ}$ and $p_{\rm L}^{\circ}$ values for accretion products of interest; P = 1atm and T = 298 K.

^a Joback method (Reid et al., 1987) ^b SPARC group contribution method (Hilal et al., 1994)

2.3.3 Extent of reaction at equilibrium (ε)

i

For the accretion ("a") and condensation ("c") reactions given in Equations (2.1) and (2.2), the overall position at equilibrium can be expressed using the extents of reaction ε_a and ε_c , respectively. In the general case,

$$\varepsilon = \Delta n_i / v_i \tag{2.11}$$

where the parameter Δn_i is the change in the number of mols of *i* relative to the initial number of mols $n_{i,0}$. For reaction (2.1), $v_A = -1$, $v_B = -1$, and $v_C = 1$. For reaction (2.2), for C_g we have $v_C = -1$, and for C_{liq} we have $v_C = 1$.

At equilibrium, the number of mols of *i* in the gas phase is given by

$$n_{i,g} = n_{i,g,0} + \sum_{j} \left(v_{i,j} \varepsilon_{a,j} \right) - \varepsilon_{c}$$
(2.12)

Equation (2.12) accounts for the possibility of multiple accretion reactions by means of the index *j*. The equation indicates that $n_{i,g}$ for any given product is affected by a single condensation ε . At equilibrium, the number of mols of *i* in the liquid phase is given by

$$\eta_{i,\text{liq}} = \varepsilon_{\text{C}} \tag{2.13}$$

wherein it is assumed that the accretion product is not present in the initial system. Table 2.3 provides the expressions for the various n_i for the case when there is only one accretion reaction.

Equilibrium values for all reactants and products are determined for a given set of $n_{i,0}$ by solving the system of equilibrium *K* expressions for the set of $\varepsilon_{a,j}$ and ε_c (In this work, the standard Excel Solver developed by Frontline Systems Inc., was used to solve the system of equilibrium *K* expressions for the set of $\varepsilon_{a,j}$ and ε_c). For reaction (2.1), $K = p_C/(p_A p_B)$. For the case of a single accretion reaction followed by condensation, when $n_{C,0}$ is zero, then *K* is expressed in ε format is

$$K_{a,1} = \frac{\varepsilon_{a,1} - \varepsilon_{c,1}}{(n_{A,0} - \varepsilon_{a,1})(n_{B,0} - \varepsilon_{a,1})} \frac{V}{RT}$$
(2.14)

Table 2.3 Initial and equilibrium amounts (mols) of each of the reactants and products in Equations (2.1) and (2.2) expressed in terms of ε (extent of reaction) values.

(Assumptions: Reactants A and B are volatile and exist only in the gas phase; the initial amount of C is zero; and the product C can exist in the gas phase, and can also condense and thereby contribute to the OPM phase.)

Compound	Initial Amount	Equilibrium Amount			
Compound		$\Delta n_{i,\mathrm{g}}$	$\Delta n_{i, \text{liq}}$	n _{i,g}	$n_{i, liq}$
А	<i>n</i> _{A,0}	- ε _{a,1}	0	<i>n</i> _{A,0} - ε _{a,1}	0
В	$n_{\mathrm{B},0}$	- ɛ _{a,1}	0	<i>n</i> _{B,0} - ε _{a,1}	0
С	0	$\epsilon_{a,1}$ - $\epsilon_{c,1}$	$\epsilon_{c,1}$	$\epsilon_{a,1}$ - $\epsilon_{c,1}$	$\epsilon_{c,1}$

When the condensation reaction (2.2) is at equilibrium, $p_{\rm C} = X_{\rm C}\zeta_{\rm C} p_{\rm L}^{\circ}$ where $X_{\rm C}$ is the mole fraction of C in the liquid PM phase, and $\zeta_{\rm C}$ is the mole-fraction-scale activity coefficient of C in the liquid PM phase (Pankow, 1994a). A version of the equilibrium constant for the condensation is then $K_{\rm c} = (p_{\rm L}^{\circ})^{-1} = \zeta_{\rm C}X_{\rm C}/p_{\rm C}$. Expressed in ε format for the case of a single accretion reaction yields

$$K_{c,1} = \frac{\zeta_C \varepsilon_{c,1}}{\varepsilon_{a,1} - \varepsilon_{c,1}} \left(\frac{1}{n_{\text{OPM}}} \right) \left(\frac{V}{RT} \right)$$
(2.15)

where n_{OPM} equals the total number of mols in the condensed phase. When the condensation of a single product C is the only source of mass in the condensed phase, then

$$n_{\rm OPM} = \varepsilon_{\rm c,1} \tag{2.16}$$

When there are multiple accretion reactions involving a single parent aldehyde, or when more than one aldehyde k is undergoing accretion reactions, n_{OPM} will be determined by an overall summation for the condensation of all accretion products plus a term (n_{na}) for those OPM-phase atmospheric compounds not related to accretion reactions:

$$n_{\rm OPM} = \sum_{k} \sum_{j} (\varepsilon_{\rm c,j})_k + n_{\rm na}$$
(2.17)

where n_{na} (mols) and OPM_{na} (µg m⁻³) are related through the mean molecular weight MW_{na} (g mol⁻¹).

2.4 Cases

The thermodynamic considerations provided here are intended to determine the extent of OPM formation at equilibrium (i.e., regardless of the time required to reach that equilibrium). We note again that such considerations will not depend on either the specific kinetic scheme, or on the presence of a catalyst, acid or otherwise. (An assumption of independence with regard to the presence of a catalyst does, however, require that the catalyst not significantly alter the activity of any constituent of interest in the PM phase.) In the application of Equations (2.16) and (2.17) in this work, it is assumed that, to a first approximation, water can be neglected as a component in an OPM

phase; separate calculations assuming water to be the primary component in the PM will also be discussed.

Five overall case types were considered (Table 2.4). The first four considered a single aldehyde together with 1-decanol. Cases 1.a-4.a and 1.b-4.b involved *n*-butanal, *n*-hexanal, *n*-octanal, and *n*-decanal, and were derived (see Appendix 1) from dark chamber experiments carried out by Jang and Kamens (2001b) in a study of how acidic seed aerosol might affect OPM formation from *n*-aldehydes. Cases 1.a-4.a considered the possible condensation of the accretion products of interest when $n_{na} = 0$. Cases 1.b-4.b considered the non-zero extent of accretion-product condensation (and thus the level of OPM that would form due to accretion reactions) when n_{na} was taken to be related to the amount of OPM reported by Jang and Kamens (2001b) for experiments conducted in the absence of acidic seed aerosol (see Appendix 1). We note that even if condensation of accretion products does not occur when $n_{na} = 0$, some condensation of the accretion products will always occur when $n_{na} \neq 0$.

The fifth case type utilized pinonaldehyde in an evaluation of the potential role of accretion reactions of natural parent aldehydes in atmospheric OPM formation. The atmospheric conditions were P = 1 atm, T = 298 K, and relative humidity (RH) = 20%. Three subcases (5.a-5.c) were considered, all of which assumed OPM_{na} = 50 µg m⁻³ with MW_{na} = 200 g mol⁻¹. Case 5.a utilized an initial value (A_0) for the pinonaldehyde concentration (0.3 µg m⁻³) that was from the upper range of the observations made by Yu et al. (1999) during a field study in Big Bear Valley (California), within the San Bernardino National Forest. Case 5.b assumed that the concentration of pinonaldehyde in the gas phase was not reduced by accretion reactions or condensation, but was held constant (e.g., by steady emissions to the air mass), with the accretion and condensation reactions then proceeding based on that steady-state concentration. Case 5.c was similar to Case 5.b, but assumed that the total levels of all pinonaldehyde-like compounds could in some cases be substantially higher than 0.3 µg m⁻³.

	A_0 (µg m ⁻³)	B_0 (µg m ⁻³)	H ₂ O @ 50% RH (µg m ⁻³)	OPM_{na} (µg m ⁻³)
Cases 1.a - 4.a Aldehydes with 1	-decanol $(n_{na} = 0)$			
1.a <i>n</i> -butanal	$2 \ge 10^4$	2×10^4	10^{7}	0
2.a <i>n</i> -hexanal	7×10^3	7×10^3	10 ⁷	0
3.a <i>n</i> -octanal	7×10^3	7×10^3	10 ⁷	0
4.a <i>n</i> -decanal	7×10^3	7 x 10 ³	10 ⁷	0
Cases 1.b - 4.b Aldehydes with 1	-decanol $(n_{na} \neq 0)$			
1.b <i>n</i> -butanal	$2 \ge 10^4$	$2 \ge 10^4$	10 ⁷	40
2.b <i>n</i> -hexanal	7×10^3	7 x 10 ³	10 ⁷	7
3.b <i>n</i> -octanal	7×10^3	7×10^3	10 ⁷	200
4.b <i>n</i> -decanal	7×10^3	7 x 10 ³	10 ⁷	200
	$\begin{array}{c} A_0 \\ (\mu g m^{-3}) \end{array}$	B_0 (µg m ⁻³)	H ₂ O @ 20% RH (µg m ⁻³)	OPM _{na} (µg m ⁻³)
Cases 5.a-5.c Pinonaldehyde (<i>n</i>	_{na} ≠0)			
5.a pinonaldehyde	0.3 (initial)	0	5 x 10 ⁶	50
5.b pinonaldehyde	0.3 (steady state)	0	5 x 10 ⁶	50
5.c pinonaldehyde- like compounds	700 (steady state)	0	5 x 10 ⁶	50

Table 2.4 Initial concentrations of *n*-aldehyde (A_0), 1-decanol (B_0), H₂O, and OPM_{na} for the five case types considered; T = 298 K.

2.5 Results and Discussion

2.5.1 Predicted OPM formation for n-aldehydes; $A_0 \approx 10,000 \ \mu g \ m^{-3}$ and $n_{na} = 0$

Jang and Kamens (2001b) reported that measurable OPM formed in a variety of high concentration *n*-aldehyde/1-decanol systems, and attributed that formation to the accretion reactions in Figure 2.1. For Cases 1.a-4.a, however, the base-case calculations carried out here predict limited extents of accretion product formation, and zero condensation of the products. Negligible formation of the Figure 2.1a accretion products is consistent with the known accretion behavior of aldehydes (see Appendix 2). The prediction of zero condensation in Cases 1.a-4.a may be understood as follows.

By analogy with dissolution of minerals into water, the general saturation index for vaporization of a multi-component liquid mixture is defined as

$$\Omega = \sum_{i} \frac{p_i}{\zeta_i p_{\mathrm{L},i}^\circ}$$
(2.18)

An equivalent version of the above equation has been discussed by Fillo et al. (2003). Consideration of evaporation/condensation process leads to the conclusions that:

$$\Omega < 1$$
 undersaturated (some evaporation of the liquid mixture will tend to occur) (2.19)

 $\Omega = 1$ saturated (system at equilibrium) (2.20)

 $\Omega > 1$ supersaturated (some condensation of the mixture will tend to occur) (2.21)

Computation of Ω requires knowledge/prediction of the individual ζ_i in the aerosol phase, and so requires knowledge/prediction of the composition of that phase. (For the calculations carried out here, it was assumed that the generally similar natures of the potentially condensable compounds permitted the approximation that $\zeta_i \approx 1$ for all compounds.) As a general example of the application of Equation (2.18), in the case of a gas phase that contains 100 compounds, each of which is present such that $p_i = 0.01 p_{L,i}^{\circ}$, adding even a small amount of any of the various *i* will supersaturate the gas phase (i.e., cause $\Omega > 1$) and allow condensation to proceed until equilibrium is reached ($\Omega = 1$).

In this work, neglecting contributions from the organic reactants, $\Omega \ll 1$ for all of the computed equilibrium positions considered in this section: $\Omega = 8 \times 10^{-5}$ (nbutanal), 6×10^{-5} (*n*-hexanal), 4×10^{-4} (*n*-octanal), and 0.3 (*n*-decanal). (In each case, the aldol accretion products in Figure 2.1b contribute essentially 100% of the value of Ω .) Moreover, the Ω values for Cases 1.a-3.a are sufficiently small that OPM formation can be ruled out even when allowing for reasonable uncertainty in the input $\Delta G_{\rm f}^{\circ}$ values for the accretion products. (Note: the $\Delta G_{\rm f}^\circ$ values for the reactants (1-decanol and the parent aldehydes) and for water are well-known.) For Case 4.a, a sensitivity test was carried out in which $\Delta G_{\rm f}^{\circ}$ values for all of the accretion products were adjusted by -10 kJ mol⁻¹ (i.e., made more stable) with the results that: 1) with all of the products assumed to remain in the gas phase, Ω was recalculated as 13; 2) the aldol condensation products again account for essentially all of that value; and 3) allowing OPM formation to proceed so that when $\Omega = 1$ then OPM $\approx 10^4 \,\mu g \, m^{-3}$. Thus, OPM formation attributable largely to aldol condensation remains a thermodynamic possibility in the *n*-decanal case. It does not appear possible at equilibrium in the *n*-butanal, *n*-hexanal, and *n*-octanal cases because while the K values for the aldol condensation reactions are similar to that for ndecanal, these three compounds do not have carbon numbers large enough to yield accretion products with sufficiently low $p_{\rm L}^{\circ}$ values to produce OPM in the systems considered here.

The fact that *n*-butanal, *n*-hexanal, *n*-octanal, and *n*-decanal have sets of *K* values for the accretion reactions in Figure 2.1 that are roughly independent of carbon number is a consequence of group contribution considerations: the incremental changes in the $\Delta G_{\rm f}^{\circ}$ values with increasing carbon number are reflected by similar changes in the $\Delta G_{\rm f}^{\circ}$ values for the products. Consequently, the reaction ΔG° values (and therefore the *K* values) are similar among these *n*-aldehydes, and also for pinonaldehyde.

2.5.2 Predicted $\triangle OPM$ formation for n-aldehydes; $A_0 \approx 10,000 \ \mu g \ m^{-3}$ and $n_{na} \neq 0$

For Cases 1.b-4.b, Jang and Kamens (2001b) give "reported ΔOPM " values ("acid-catalyzed" vs. "non-acid-catalyzed", see Table A.1.2.) of: 4 (*n*-butanal), 34 (*n*-hexanal), 131 (*n*-octanal), and 55 (*n*-decanal) µg m⁻³. Figure 2.2 compares those "reported ΔOPM " values with the "predicted ΔOPM " values obtained here. The latter, computed as the difference [(total OPM predicted to form in the presence of the initial n_{na} value) - (OPM corresponding to the initial n_{na})] were: 0.0017 (*n*-butanal), 0.00037 (*n*-hexanal), 0.86 (*n*-octanal), and 99 (*n*-decanal) µg m⁻³. By analogy with the $n_{na} = 0$ cases: 1) the relatively high p_L° values of the lower carbon number aldol condensation products do not allow condensation of significant percentages of the product amounts that do form; and 2) only with decanal does the "predicted ΔOPM " value approximate the "reported ΔOPM " from the experiments of Jang and Kamens (2001b). (The essential equivalence in Figure 2.2 between the $\Pi_{\alpha,\beta-unsaturated carbonyl}$ values calculated for the aldol condensation reaction and the "predicted ΔOPM " values is a consequence of the limited extent of that reaction (i.e., non-depletion of the initial reactant *p* values) in these cases.)

As noted, the above "predicted $\triangle OPM$ " values were calculated assuming a strictly organic PM phase with all $\zeta_i = 1$. Ambient atmospheric PM, however, may contain considerable water as well as other constituents in one or more phases (Pankow, 2003; Griffin et al., 2003; Erdakos and Pankow, 2004). To consider the possible effects of a mostly water PM phase, the "predicted $\triangle OPM$ " was recalculated for Case 4.b (*n*-decanal) assuming that the initial, "non-acid catalyzed" PM was primarily water. Values of ζ_i for the organic reactants and products in water were extracted from $p_{L,i}^{\circ}$ values and air/water partitioning coefficients obtained from SPARC (Hilal et al., 1994); ζ_{water} was assumed to be unity. Because $\zeta_i >> 1$ for all of the organic compounds, only negligible condensation of the organic reactants and products was found to occur, giving "predicted $\triangle OPM$ " ≈ 0 . Significant enhancement of the partitioning due to presence of H₂SO₄ in a partially aqueous PM phase can also be ruled out.



Figure 2.2 Measured $\triangle OPM$ (Jang and Kamens, 2001b) vs. predicted $\triangle OPM$.

This is because of the exceedingly weak basicity of aldehydes (Lee et al., 2002) and of ketones (Noziere and Riemer, 2003). For example, for acetone and pentanedione protonation will not cause significant partitioning to acidic aqueous solutions, even with very concentrated aqueous H_2SO_4 solutions (Noziere and Riemer, 2003).

2.5.3 Predicted OPM formation for pinonaldehyde and pinonaldehyde-like compounds at varying A_0 ; $n_{na} \neq 0$

The pinonaldehyde hydrate, oligomers, hemiacetal, and acetal are not thermodynamically favored in the atmosphere under relevant conditions. This is because the K values for their formation are similar to the K values for the corresponding products from the *n*-aldehydes. Therefore, the calculations for Cases 5.a-5.c only considered formation of the aldol products and their condensation into the assumed background OPM of 50 μ g m⁻³. However, even in Case 5.b in which the pinonaldehyde concentration was assumed to remain constant at an environmentally-relevant level of 0.3 µg m⁻³ and not depleted by aldol reactions, the predicted added OPM was found to be low (~ 2×10^{-6} μ g m⁻³); lowering the system T to 288 K does not alter this conclusion. Only after the level of pinonaldehyde (or total pinonaldehyde-like compounds) is increased to a steadystate (i.e., non-depleted) level of $\sim 700 \ \mu g \ m^{-3}$ does the predicted condensation of pinonaldehyde-like aldol products approach 10 µg m⁻³. Allowing for uncertainty in the input $\Delta G_{\rm f}^{\circ}$ values of +10 kJ mol⁻¹ for pinonaldehyde and -10 kJ mol⁻¹ for its aldol products does not reduce the required steady-state total "pinonaldehyde-like" concentration below $\sim 2 \ \mu g \ m^{-3}$. Since total non-methane (NM) atmospheric VOC levels have been reported to be in the range 10-700 µg m⁻³ (Mohamed et al., 2002; Schauer et al., 2002), with total aldehydes only a very small fraction of total NMVOCs, significant OPM formation by aldol condensation of pinonaldehyde-like compounds does not seem to be thermodynamically favored in the atmosphere.

2.6 References

- Bridgeman, O.C., Aldrich, E.W., 1964. Vapor pressure tables for water. *Journal of Heat Transfer*. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, March 2003. National Institute of Standards and Technology, Gaithersburg. (http://webbook.nist.gov, viewed: June, 2003).
- Erdakos, G.B., Pankow, J.F., 2004. Gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles. 2. Phase separation in liquid particulate matter containing polar and low-polarity organic compounds. *Atmospheric Environment* 38, 1005-1013.
- Fillo, J.D., Koehler, C.A., Nguyen, T.P., De Haan, D.O., 2003. Simulating secondary organic aerosol activation by condensation of multiple organics on seed particles. *Environmental Science and Technology* 37, 4672-4677.
- Griffin, R.J., Nguyen, K., Dabdub, D., Seinfeld, J. H., 2003. A coupled hydrophobichydrophilic model for predicting secondary organic aerosol formation. *Journal of Atmospheric Chemistry* 44, 171-190.
- Hilal, S.H., Carreira, L.A., Karickhoff, S.W., 1994. Estimation of chemical reactivity parameters and physical properties of organic molecules using SPARC. In: Murray, J.S. (Ed.), Quantitative Treatments of Solute/Solvent Interactions. Elsevier, Amsterdam, pp. 293-353.
- Jang, M., Kamens, R.M., 2001a. Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environmental Science and Technology* 35, 3626-3639.
- Jang, M., Kamens, R.M., 2001b. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology* 35, 4758-4766.
- Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* 298, 814-817.
- Kamens, R.M., Jaoui, M., 2001. Modeling aerosol formation from α -pinene + NO_x in the presence of natural sunlight using gas-phase kinetics and gas-particle partitioning theory. *Environmental Science and Technology* 35, 1394-1405.
- Lee, I., Uhm, T.S., Ryu, Z.H., Koo, I.S., Lee, J.P., 2002. Transmission of substituent effects in the protonation of substituted 2-furaldehydes in sulfuric acids. *Bulletin of the Korean Chemical Society* 23, 758-760.

- Mohamed, M.F, Kang, D., Aneja, V.P., 2002. Volatile organic compounds in some urban locations in United States. *Chemosphere* 42, 863-882.
- Noziere, B., Riemer, D.D., 2003. The chemical processing of gas-phase carbonyl compounds by sulfuric acid aerosols: 2,3-pentanedione. *Atmospheric Environment* 37, 841-851.
- Pankow, J.F., 1994a. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185-188.
- Pankow, J.F., 1994b. An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* 28, 189-193.
- Pankow, J.F., Seinfeld, J.H., Asher, W.E., Erdakos, G.B., 2001. Modeling the formation of secondary organic aerosol. 1. Application of theoretical principles to measurements obtained in the α -pinene-, β -pinene-, sabinene-, Δ^3 -carene-, and cyclohexene-ozone systems. *Environmental Science and Technology* 35, 1164-1172.
- Pankow, J.F., 2003. Gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles. 1. Unified modeling framework. *Atmospheric Environment* 37, 3323-3333.
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. Properties of Gases and Liquids, 4th ed. McGraw-Hill, New York. pp.741.
- Schauer, J.J., Fraser, M.P. Cass, G.R., Simoneit, B.R.T., 2002. Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. *Environmental Science and Technology* 36, 3806-3814.
- Seinfeld, J.H., Erdakos, G.B., Asher, W.E., Pankow, J.F., 2001. Modeling the formation of secondary organic aerosol. 2. The predicted effects of relative humidity on aerosol formation in the α -pinene-, β -pinene-, sabinene-, Δ^3 -carene-, and cyclohexene-ozone systems. *Environmental Science and Technology* 35, 1164-1172.
- Tobias, H.J., Ziemann, P.J., 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environmental Science and Technology* 34, 2105-2115.
- Yaws, C.L., 1999. Chemical Properties Handbook. McGraw-Hill, New York, pp. 600.

Yu, J., Griffin, R.J., Cocker III, D.R., Flagan, R.C., Seinfeld, J.H., 1999. Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. *Geophysical Research Letters* 26, 1145-1148.

CHAPTER 3

Thermodynamics of the Formation of Atmospheric Organic Particulate Matter by Accretion Reactions: Dialdehydes and Diketones

3.1 Introduction

Predicting the formation of organic particulate matter (OPM) in the atmosphere by absorptive gas/particle (G/P) partitioning requires a knowledge of the identities, quantities, and properties of all partitioning compounds (Pankow, 1994a,b). Unfortunately, efforts to identify and quantify the numerous components found in samples of actual atmospheric OPM have met with marginal success: molecular level characterizations of OPM samples usually account for only 10-20% of the OPM mass (e.g., Rogge et al., 1993; Mazurek, 2002). Limiting the level of component identification simply to the number of carbon atoms in OPM constituents (e.g., C_{20}) can increase the fraction of the "identified mass", but such studies can still only account for a maximum of ~50% of the mass (Mazurek et al., 1997).

While complexity alone undoubtedly causes a large portion of the problem of identifying and quantifying the numerous constituents present in atmospheric OPM samples, another portion is related to the presence of difficult-to-determine, high-molecular weight (MW)/low-volatility compounds. The view that atmospheric OPM can contain constituents of relatively high MW is consistent with the visual appearance of a well-loaded, urban air filter. For example, "primary" emissions of polycyclic aromatic hydrocarbons (PAHs) of intermediate to very high MW can result from the polymerization of gaseous acetylene units during combustion, with elemental ("black") carbon the consequence of extended polymerization (Commins, 1969; Richter and Howard, 2000).

The original theory of absorptive G/P partitioning (Pankow, 1994a,b) explicitly allows that a portion of the absorptive fraction of an atmospheric PM sample can be comprised of organic constituents that are essentially "non-volatile". Haagen-Smit (1952) can be credited with the first recognition that high MW, "*nonvolatile products*" are likely to form during "secondary" reactions in the atmosphere, e.g., the polymerizing action of photochemically-produced peroxides on unsaturated organic compounds such as cyclohexene. More recently, various lines of physical evidence have emerged suggesting that at least some portion of the OPM formed in chamber studies is comprised of relatively high MW oligomers (e.g., Gao et al., 2004; Iinuma et al., 2004; Jang et al., 2002; Kalberer et al., 2004; Limbeck et al., 2003; Tobias and Ziemann, 2000; Tolocka et al., 2004). And, evidence for high MW polycarboxylic acids in the atmosphere is available (e.g., Havers et al., 1998; Mukai and Ambe, 1986; Samburova et al., 2005; Zappoli et al., 1999).

The above discussion indicates that when it occurs, the chemical kinetic movement of some of the organic carbon in the atmosphere from relatively volatile compounds to lower-volatility compounds is certain to be quite complicated. The theory of Pankow (1994a,b), nevertheless, allows time-dependent equilibrium OPM levels to be computed for any series of "snap-shot" positions as a mix of condensable compounds arising from primary emissions and/or the ambient oxidation of volatile organic compounds (VOCs) changes to another mix of compounds by oxidation and other reactions. Also, despite some confusion in the literature, the Pankow (1994a,b) conceptual model does not assume that once a condensable compound is in the OPM phase, no further chemical reaction could occur therein.

The simple oligomerization/polymerization of a single type of monomer molecule (e.g., A) is not the only route to higher–MW OPM constituents. Since a wide variety of different types of reactions and cross reactions can occur among molecules A, B, etc., the term "accretion reactions" has been proposed for use in general discussions of MW-building reactions. (Simple oxidation reactions are excluded from the "accretion reaction" category, see Section 2.1) Given the complexity of the atmospheric constituent mix, innumerable accretion products are possible. Moreover, since each accretion product is certain to be subject to a range of subsequent oxidation reactions,

it becomes readily apparent why the molecular level characterization of atmospheric OPM is difficult

A general theoretical approach exists for evaluating the thermodynamic feasibilities of accretion reactions and the extents to which their products may contribute to OPM formation. If the product C is presumed to be a relatively low vapor pressure compound, then the gaseous compounds A and B may form OPM according to:

$$A_g + B_g \leftrightarrow C_g$$
 accretion in the gas phase, then (3.1)

$$C_g \leftrightarrow C_{liq}$$
 G/P equilibration of accretion product (3.2)

Other reaction schemes can convert A and B into C_{liq} , including schemes in which the nascency of C occurs within, or at the surface of, an OPM phase. All reaction schemes that begin with the same reactants and end with the same products are thermodynamically equivalent. Unlike kinetic analyses (how fast reactions may occur), thermodynamic analyses (extents to which reactions may occur) depend only on the initial and final states. Thus, all conclusions regarding thermodynamic favorability and possible extent of OPM formation remain independent of the scheme by which an accretion reaction actually proceeds, or whether an acid/base catalyst is present.

Table 3.1 summarizes major types, formation reactions, and linkages of accretion products of proposed importance in the atmosphere. In the thermodynamic considerations of simple monoaldehydes and monoketones discussed in Chapter 2, it was concluded that: a) neither hydration/polymerization nor hemiacetal/acetal formation are sufficiently thermodynamically favorable to require inclusion among accretion reactions considered important to OPM formation in the atmosphere; b) aldol condensation reactions of monoaldehydes may be important under some circumstances.

This chapter focuses on dialdehydes, methylglyoxal, and diketones. Being difunctional, compounds of these types hold increased potential for undergoing OPM– relevant reactions, as compared to monoaldehydes and monoketones of the same general chain length. The theoretical approach introduced in Section 2.2, and further described herein, is utilized to consider accretion reactions of six dicarbonyl reactants: glyoxal, methylglyoxal, 1,4-butanedial, 1,6-hexanedial, 2,3-butanedione, and 2,5-hexanedione.

The accretion products of potential interest are summarized in Figures 3.1 and 3.2, and Tables 3.2 and 3.3 (product types and linkages).

3.2 Theory

The use of thermodynamic principles to evaluate the tendency of a given accretion reaction to contribute to atmospheric OPM has been discussed in Chapter 2. Of governing importance is the equilibrium constant *K* for the accretion reaction. The value of *K* is determined by the free energy of reaction, $\Delta G^{\circ} (= \sum_{i} v_i \Delta G^{\circ}_{f,i})$ according to

$$\Delta G^{\rm o} = -RT \ln K \tag{3.3}$$

where v_i is the stoichiometric coefficient for compound *i* in the accretion reaction, $\Delta G_{f,i}^{\circ}$ (kJ mol⁻¹) is the standard free energy of formation for *i*, *R* (8.314 x 10⁻³ kJ mol⁻¹ K⁻¹) is the ideal gas constant, and *T* is temperature (K). In addition to *K*, the overall tendency for an accretion reaction to contribute to OPM depends on three other factors (see Section 2.2.2): 1) the concentration driving force for product formation provided by the initial gas-phase pressures p_A and p_B (atm) of the reactants A and B; 2) the tendency for C to condense, as set in part by its pure-liquid vapor pressure p_L° (atm) and specifically determined by the equilibrium constant K_p (m³µg⁻¹) for partitioning of C between the gas and OPM phases; and 3) OPM_{na} (µg m⁻³), the initial non-accretion related OPM concentration into which the condensation of C must first occur.

Accretion Reaction and Product Type	Linkages	Relevance for OPM Formation [Chapter]
aldehyde/ketone + water = monomer	gem-diol	small [2]
<i>n</i> aldehyde/ketone + <i>m</i> water = oligomer	ether	small [2]
aldehyde/ketone + 1/2 alcohol = monomer	hemiacetal/acetal	small [2]
2 aldehyde/ketone = oligomer	aldol	small [2]
2 aldehyde/ketone = oligomer + water	alkene	small (potentially relevant at high concentrations of reactant carbonyl) [2]
dialdehyde/diketone + m water = monomer	gem-diol	? [3]
2 dialdehyde/diketone + m water = oligomer	hemiacetal/acetal	? [3]
dialdehyde/diketone + m alcohol = monomer	hemiacetal/acetal	? [3]
2 dialdehyde/diketone = oligomer	aldol	? [3]
2/3 dialdehyde/diketone = oligomer + $1/2$ water	alkene, aldol	? [3]
n hydroxy acid = oligomer + n -1 water	ester	? [4]

Table 3.1 Major types of accretion products and their formation reactions, types of linkages, and relevance for organic particulate matter (OPM) formation in the atmosphere.

Table 3.1 cont. Major types of accretion products and their formation reactions, types of linkages, and relevance for organic particulate matter (OPM) formation in the atmosphere.

Accretion Reaction and Product Type	Linkages	Relevance for OPM Formation [Chapter]
acid + alcohol = monomer + water	ester	? [4]
$n \operatorname{diacid} + m \operatorname{diol} = \operatorname{oligomer} + (n + m - 1) \operatorname{water}$	ester	? [4]
acid + amine = monomer + water	amide	? [4]
n diacid + m amine = oligomer + $(n + m - 1)$ water	amide	? [4]



Figure 3.1 Accretion products of potential interest for glyoxal. Corresponding accretion products were considered for methylglyoxal (m.1-m.18), 1,4-butanedial (ba.1-ba.18), 1,6-hexanedial (ha.1-ha.18), 2,3-butanedione (bo.1-bo.18), and 2,5-hexanedione (ho.1-ho.18).



Figure 3.2 Accretion products of potential interest for 1,4-butanedial. Corresponding accretion products were considered for methylglyoxal (m.19-m.22), 1,6-hexanedial (ha.19-ha.22), 2,3-butanedione (bo.19-bo.22), and 2,5-hexanedione (ho.19-ho.22).

Reactant Dicarbonyl	Accretion Product
glyoxal	g.1-g.18
methylglyoxal	m.1, m.1', m.2, m.2', m.3, m.4, m.4', m.5, m.6, m.6', m.7, m.8, m.8', m.8'', m.10, m.10', m.11, m.11', m.12, m.12', m.12'', m.14, m.15, m.15', m.15', m.16, m.16', m.16'', m.16''', m.17, m.17', m.17'', m.18, m.18', m.19, m.19', m.20, m.20', m.21, m.21', m.22
1,4-butanedial	ba.1-ba.22
1,6-hexanedial	h.1-h.22
2,3-butanedione	bo.1-bo.8, bo.10-bo.12, bo.14-bo.22
2,5-hexanedione	ho.1-ho.8, ho.10-ho.12, ho.14-ho.22

 Table 3.2 Summary of reactants and accretion products of potential interest.

', ", and " indicate isomers

Accretion Product	Accretion Product Type	Linkage(s)
1, 1′	monomer	hemiacetal
2, 2'	monomer	acetal
3	monomer	hemiacetal
4, 4′	monomer	hemiacetal, acetal
5	monomer	acetal
6, 6'	monomer	gem-diol
7	monomer	gem-diol
8a-c, 8'a-c, 8"a-c	dimer	hemiacetal
9a-c	dimer	acetal
10a,b; 10'a,b	dimer	hemiacetal/acetal
11, 11′	dimer	hemiacetal
12a-c, 12'	trimer	hemiacetal
13а-с	trimer	acetal
14	trimer	hemiacetal/acetal
15a-c, 15'a-c, 15"a-c	trimer	hemiacetal/acetal
16a,b; 16'a,b; 16"a,b; 16""a,b	trimer	hemiacetal/acetal
17, 17′, 17″	trimer	hemiacetal/acetal
18a-d, 18'a-d	trimer	ether
19, 19′	dimer	aldol
20, 20'	dimer	alkene
21, 21′	trimer	alkene, aldol
22	trimer	alkene

Table 3.3 Summary of accretion products, types, and linkages.

', ", and " indicate isomers

3.3 Mathematical Solution Process

3.3.1 Estimation of vapor pressures (p_L^o) and free energies of formation (ΔG_f^o)

Values of $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ were obtained from the literature whenever available; otherwise, they were estimated. Needed $p_{\rm L}^{\circ}$ values were estimated using the SPARC method (Hilal et al., 1994). Needed $\Delta G_{\rm f}^{\circ}$ values were estimated using the group contribution method of Benson (1976). Poling et al. (2001) found the Benson method (1976) to be the most accurate of several methods tested for estimating $\Delta G_{\rm f}^{\circ}$ values, yielding an average unsigned error of 6% for published $\Delta G_{\rm f}^{\circ}$ values of 27 organic compounds, with 78% of the estimated values characterized by an unsigned error of less than 10%. The largest errors were found to occur when the absolute value $|\Delta G_{\rm f}^{\circ}| < 10$ kJ mol⁻¹; when $|\Delta G_{\rm f}^{\circ}| > 10$ kJ mol⁻¹, the average unsigned error was 3%, with 84% of the estimated values characterized by an unsigned error of less than 10%.

The method of Benson (1976) was implemented here using the CHETAH (2002) algorithm. For molecular groups not included in the CHETAH (2002) database, or simply lacking known enthalpy of formation ($\Delta H_{\rm f}^{\circ}$) and/or entropy (S°) values (see Table 3.4), $\Delta H_{\rm f}^{\circ}$ and S° values were estimated by linear interpolation as described by Frurip et al. (2002); the associated errors are reported as being less than ±8 kJ mol⁻¹, and less than ±4 J mol⁻¹ K⁻¹, respectively (Frurip et al., 2002). CHETAH (2002) considers the effects of structural rings on $\Delta G_{\rm f}^{\circ}$ values by means of ring correction terms for $\Delta H_{\rm f}^{\circ}$ and S° . In this work, for products with rings not found in the CHETAH (2002) database, values of the correction terms were chosen based on ring similarity and so that $\Delta G_{\rm f}^{\circ}$ would be minimized.

Group: Benson Notation	Group: Physical Description	$\Delta H_{\rm f}^{\circ}~({\rm kJ~mol}^{-1})$	S° (J mol ⁻¹ K ⁻¹)
C-(=C,2O,C)	C singly bonded to 1 C=, 1 O, 1 O, and 1 C	-72.8	-148
C-(20,C0,C)	C singly bonded to 2 O, 1 C=O, and 1 C	-74.1	-141
CH-(=C,2O)	C singly bonded to 1 H, 1 C=, and 2 O	-66.5	-47
CH-(=C,O,C)	C singly bonded to 1 H, 1 C=, 1 O, and 1 C	-28.5	-44
CH-(=C, CO,C)	C singly bonded to 1 H, 1 C=, 1 C=O, and 1 C	-5.4	-49
CH-(20,CO)	C singly bonded to 1 H, 2 O, and 1 C=O	-67.4	-48
CH2-(=C,CO)	C singly bonded to 2 H, 1 C=, and 1 C=O	-15.9	45
CO-(=C,CO)	C doubly bonded to 1 O (C=O), and singly bonded to 1 C= and 1 C=O	-109.2	68

Table 3.4 Molecular groups with $\Delta H_{\rm f}^{\circ}$ and S° data unavailable in the CHETAH (2002) database and their interpolated $\Delta H_{\rm f}^{\circ}$ and S° values; carbon: C, doubly bonded carbon: C=, hydrogen: H, oxygen: O, carbonyl: C=O.

3.3.2 Mass Balance

Mass balance considerations lead to

$$A_{0} = A_{g} + A_{liq} + \sum_{i=1}^{N} \left(C_{i,g} \times \frac{\nu_{A} M W_{A}}{\nu_{C,i} M W_{C,i}} \right) + \sum_{i=1}^{N} \left(C_{i,liq} \times \frac{\nu_{A} M W_{A}}{\nu_{C,i} M W_{C,i}} \right)$$
(3.4)

where for simplicity we allow that A_g and A_{liq} can denote the *concentrations* (µg m⁻³) of A in the gas and liquid phases, as well as simply A in the gas and liquid OPM phases (see Equation (3.1)). Similarly, we allow $C_{i,g}$ and $C_{i,liq}$ to represent the gas- and liquid-phase concentrations (µg m⁻³) of the *i*th product C. The parameter *N* is the number of possible products from A. Each v is an overall stoichiometric coefficient (does not carry sign) for production of C_i from A, and each MW (g mol⁻¹) is a molecular weight. Equation (3.4) is a simple representation of mass balance that is valid for any system arising from the initial value A₀.

Under conditions of equilibrium for the accretion and condensation reactions,

$$A_{liq}/A_g = K_{p,A} OPM$$
(3.5)

and

$$C_{i,liq}/C_{i,g} = K_{p,C_i} OPM$$
(3.6)

For an accretion reaction following the form of Equation (3.1), when the gas-phase concentration of B is assumed to be held constant at $n_{\rm B}/V$, we have:

$$C_{g} = K \times A_{g} \times \left(\frac{V}{10^{6} \text{ MW}_{A}}\right) \times \left(n_{B}\left(\frac{RT}{V}\right)\right) \times \left(\frac{V}{10^{6} \text{ MW}_{C}}\right)^{-1} = \frac{KA_{g}n_{B}RTMW_{C}}{MW_{A}V}$$
(3.7)

where $V(m^3)$ is the volume of the gas phase, and the terms *RT/V* and *V/(10⁶MW)* provide necessary unit conversions from mols to µg m⁻³. Analogs of Equation (3.7) can be written for accretion reactions with stoichiometries different from that of Equation (3.1). After substitution of Equations (3.4-3.6), Equation (3.7) can be solved for A_g given values of the other parameters. In this work, mass balance equations were solved using the standard Excel Solver (developed by Frontline Systems, Inc.), implemented through a subroutine written in Visual Basic.

3.4 Cases

For each of the dicarbonyl reactants (glyoxal, methylglyoxal, 1,4-butanedial, 1,6hexanedial, 2,3-butanedione, and 2,5-hexanedione), a range of initial gas-phase concentration values A_0 (10⁻³ to 10⁴ µg m⁻³) and relative humidity (RH) were considered. Each case utilized a constant concentration of 1-decanol (10 µg m⁻³). It was assumed that P = 1 atm and T = 298 K. The effects of RH on accretion product formation were examined for a range of RH (10 to 90%) using a single A_0 value (10 µg m⁻³). The modeling of the G/P partitioning (i.e., condensation) of the accretion products occurred with activity coefficients (ζ) ≈ 1 for all products in the OPM phase. (This assumption was considered reasonable given that: a) we are interested in understanding when significant new OPM will form; and b) when that does occur, the resulting overall OPM will be composed largely of the condensed accretion products themselves. See Section 2.5.2 for further discussion.) Lastly, the modeling assumed that the OPM present would only absorb a relatively small amount of water, which is consistent with the results of Seinfeld et al. (2001).

3.5 Results and Discussion

3.5.1 Predicted OPM formation; $A_0 = 10^{-3}$ to $10^4 \mu g m^{-3}$ and RH = 20%

Figure 3.3 illustrates the OPM levels predicted to form when the accretion products for each reactant dicarbonyl are as listed in Table 3.2, with 1-decanol held at 10 μ g m⁻³ and A₀ ranging from 10⁻³ to 10⁴ μ g m⁻³. The range selected for A₀ more than encompasses available ambient values for relevant compounds. For example, in a forested area in Japan, Matsunaga et al. (2004) measured a range of biogenic aldehydes, hydroxy carbonyls, and dicarbonyls; the single highest gas-phase concentration found was 0.63 μ g m⁻³ (4-oxopentenal). For urban air, Grosjean et al. (1996) and Grosjean et al. (2002) reported concentrations of 0.36-0.78 μ g m⁻³ for glyoxal and 1.04-1.82 μ g m⁻³ for methylglyoxal; for a severe smog episode during a study of major gas and particle



Figure 3.3 Predicted total additional OPM for each dicarbonyl reactant as a function of initial dicarbonyl concentration, A_0 .

phase organic compounds in California's South Coast Air Basin, Fraser et al. (2000) reported levels of 2.4 μ g m⁻³ for glyoxal and 3.7 μ g m⁻³ for methylglyoxal.

The calculations performed in this study were made for an initial background OPM level of 15 μ g m⁻³. Any compound that can give rise to ~1% of that value is of interest from a mass-based perspective (compounds with lower mass concentrations may be important from a health-based perspective). For $A_0 = 10 \ \mu g \ m^{-3}$, among the dicarbonvl reactants considered here, glyoxal ($1.5 \times 10^{-1} \,\mu g \, m^{-3}$) and methylglyoxal ($1.4 \times 10^{-1} \,\mu g \, m^{-3}$) ³) meet that criterion. The formation of OPM by glyoxal and methylglyoxal at this A_0 is a consequence of essentially complete conversion to products that condense to a small extent into the liquid-OPM phase: for glyoxal, the dominant product is the diol ($p_{\rm L}^{\circ} \approx 10^{-10}$ ⁷ atm), and for methylglyoxal it is an aldol (m.19, $p_{\rm L}^{\circ} \approx 10^{-7}$ atm) (see Figures 3.4 and 3.5). The prediction of diol formation and subsequent oligomerization by glyoxal is consistent with observations made by Liggio et al. (2005). (Glyoxal cannot undergo aldol reactions because of the adjacency of its two terminal aldehyde groups.) In a supplementary consideration utilizing the unsaturated dicarbonyl 4-oxo-pentenal, the dominant accretion reactions for glyoxal and methylglyoxal were not found to be likely contributors to atmospheric OPM; however, other reactions of such compounds may be important.

While an initial total dialdehyde concentration of 10 µg m⁻³ is likely near the upper end of what may be observed in the atmosphere, A₀ values as high as ~10⁴ µg m⁻³ have been used in chamber experiments (e.g., Jang and Kamens, 2001). In that case, for the reactant carbonyls considered here, the predicted levels of additional OPM are: 9.0 ×10³ (methylglyoxal), 8.8 ×10³ (1,6-hexanedial), 8.4 ×10³ (glyoxal), 4.3 ×10³ (1,4-butanedial), 1.7 ×10⁻¹ (2,3-butanedione), and 1.7 ×10⁻³ µg m⁻³ (2,5-hexanedione). The greatly increased OPM formation for glyoxal at A₀ = 10⁴ µg m⁻³ vs. 10 µg m⁻³ is a consequence of the significant formation of low p_L° oligomers of the diol (e.g., the dimer g.8a for which $p_L^{\circ} \approx 10^{-9}$ atm).



Figure 3.4 Dominant accretion products of glyoxal for $A_0 = 10^{-3}$ to 10^4 (refer to Figure 3.1 for accretion product structures).



Figure 3.5 Dominant accretion products of methylglyoxal for $A_0 = 10^{-3}$ to 10^4 (refer to Figures 3.1 and 3.2 for accretion product structures).

For 1,6-hexanedial and 1,4-butanedial, while conversion to any of the accretion products considered is not favored at $A_0 = 10 \ \mu g \ m^{-3}$, the *K* values for aldol condensation of these dialdehydes are sufficiently large that significant additional OPM can form when A_0 is high (see Figure 3.3). The fact that the diketones are predicted to have little OPM formation potential by the accretion reactions considered here is analogous to observations made in Sections 2.5.1 and 2.5.2 for monoketones.

3.5.2 Predicted OPM formation; $A_0 = 10 \mu g m^{-3}$ and RH = 10-90%

Figure 3.6 illustrates the relationship between RH and predicted total additional OPM for each reactant dicarbonyl at $A_0 = 10 \ \mu g \ m^{-3}$. For glyoxal, methylglyoxal, 1,4butanedial, and 1,6-hexanedial, as RH values increase, predicted total additional OPM levels decrease due to: 1) an increased favorability of the diols over more condensable accretion products (i.e., m.19, ba.20, ha.22); and 2) a decreased favorability of the condensable accretion products for which water is a co-product. For 2,3-butanedione and 2,5-hexanedione, as RH values increase, the increased favorability of the diols leads to greater conversion of reactant to accretion product, and thus, predicted total additional OPM levels increase. Overall, for the reactants considered here, RH is not a critical variable: the reactants that show strong dependence on RH do not possess much OPM formation potential by the accretion product routes considered here; for those that do show such a potential, the dependence on RH is weak.

3.5.3 Uncertainties in $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ values: implications for predicted OPM formation

The predicted OPM levels were considered in a sensitivity analysis that employed variations of the input parameters (see Table 3.5). For Case 1, the UNIFAC- $p_{\rm L}^{\circ}$ method of Asher et al. (2002) was used in place of SPARC to estimate $p_{\rm L}^{\circ}$ values.



Figure 3.6 Predicted total additional OPM for each dicarbonyl reactant as a function of relative humidity (RH), with $A_0 = 10 \ \mu g \ m^{-3}$.
$-15 \ \mu g \text{ m}$, KH -20% , and $T - 298 \text{ K}$.				
	"Base Case": SPARC	Case 1: UNIFAC- $p_{\rm L}^{\circ}$	Case 2: SPARC/ by varying ΔG° , <i>K</i> adjusted to favor products	Case 3: SPARC/ by varying ΔG° , <i>K</i> adjusted to favor reactants
glyoxal	1.5 x 10 ⁻¹	1.5 x 10 ⁻²	1.2 x 10 ⁻¹	4.7 x 10 ⁻²
methylglyoxal	1.4 x 10 ⁻¹	1.2 x 10 ⁻¹	1.1 x 10 ⁻¹	2.3 x 10 ⁻²
1,4-butanedial	6.4 x 10 ⁻⁶	1.0 x 10 ⁻⁴	3.1 x 10 ⁻³	2.2 x 10 ⁻⁹
1,6-hexanedial	9.1 x 10 ⁻³	9.2 x 10 ⁻³	8.6 x 10 ⁻¹	1.1 x 10 ⁻⁷
2,3-butanedione	4.1 x 10 ⁻⁶	4.9 x 10 ⁻⁷	4.8 x 10 ⁻³	3.3 x 10 ⁻¹⁰
2,5-				
hexanedione	4.7 x 10 ⁻⁹	5.2 x 10 ⁻⁷	6.3 x 10 ⁻⁵	$4.6 \ge 10^{-13}$

Table 3.5. Predicted additional OPM levels ($\mu g m^{-3}$) for "base case" and three additional cases. Emboldened values meet criterion described in section 3.5.1: a compound that can give rise to ~1% of initial background OPM is of interest. Values here are for OPM_{na} = 15 $\mu g m^{-3}$, RH = 20%, and T = 298 K.

For Cases 2 and 3, the effects of adjusting the *K* values for accretion product formation were considered by varying the $\Delta G_{\rm f}^{\circ}$ values of all reactants and dominant products (except for glyoxal and water whose $\Delta G_{\rm f}^{\circ}$ values are well known) as follows: Case 2) all reactants up by 3% and all products down by 3%; and Case 3) vice versa. Case 2 increases *K* and favors the products. Because Case 3 decreases *K* and favors the reactants, the calculated levels of additional OPM are smaller than in Cases 1 and 2, and will not be discussed further.

For glyoxal in Case 1, relative to the base case, there is a tenfold decrease in predicted additional OPM (the p_L° values for the dominant accretion products (g.6 and g.8a) from the UNIFAC- p_L° method are 10 and 1000 times higher (respectively) than those from SPARC). In Case 2, adjusting ΔG_f° for both the diol and dimer g.8a to favor product formation results in an increase in the favorability of the diol over the dimer, leading to a decrease in the formation of the more condensable dimer, and therefore, a decrease in predicted additional OPM. Similar results are observed for methylglyoxal in Case 2: the diol becomes the dominant accretion product over the more condensable aldol m.19, resulting in a decrease in predicted additional OPM. Based on the additional OPM criterion discussed in Section 3.1, at $A_0 = 10 \ \mu g \ m^{-3}$, the Table 3.5 results suggest that accretion reactions of glyoxal, methylglyoxal, and possibly 1,6-hexanedial could lead to substantive levels of additional OPM.

3.6 References

- Asher, W.E., Pankow, J.F., Erdakos, G.B., Seinfeld, J.H., 2002. Estimating the vapor pressures of multi-functional oxygen-containing organic compounds using group contribution methods. *Atmospheric Environment* 36, 1483-1498.
- Barsanti, K.B., Pankow, J.F., 2004. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 1: Aldehydes and ketones. *Atmospheric Environment* 38, 4371-4382.
- Benson, S.W., 1976. Thermochemical Kinetics. Wiley, New York, pp. 336.
- CHETAH Version 7.3: The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (CHETAH), 2002. ASTM International, Pennsylvania.
- Commins, B.T., 1969. Formation of polycyclic aromatic hydrocarbons during pyrolysis and combustion of hydrocarbons. *Atmospheric Environment* 3, 565-572.
- Fraser, M.P., Kleeman, M.J., Schauer, J.J., Cass, G.R., 2000. Modeling the atmospheric concentrations of individual gas-phase and particle-phase organic compounds. *Environmental Science and Technology* 34, 1302-1312.
- Frurip, D., Downey, J.R., LaBarge, M., 2002. Estimation of Missing Group Data of Organic Species for Use in the CHETAH Program. ASTM International, Pennsylvania.
- Gao, S., Keywood, M., Ng, N.L., Surratt, J., Varutbangkul, R.B., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004. Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α-pinene. *Journal of Physical Chemistry A* 108, 10147-10164.
- Grosjean, D., Grosjean, E., Moreira, L.F., 2002. Speciated ambient carbonyls in Rio de Janeiro, Brazil. *Environmental Science and Technology* 36, 1389-1395.
- Grosjean, E., Grosjean, D., Fraser, M.P., Cass, G.R., 1996. Air quality model evaluation data for organics. 2. C₁-C₁₄ carbonyls in Los Angeles air. *Environmental Science and Technology* 30, 2687-2703.
- Haagen-Smit, A.J., 1952. Chemistry and physiology of Los Angeles smog. *Industrial Engineering and Chemistry* 44, 1342-1346.
- Havers, N., Burpa, P., Lambert, J., Klockow, D., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *Journal of Atmospheric Chemistry* 29, 45-54.

- Hilal, S.H., Carreira, L.A., Karickhoff, S.W., 1994. Estimation of chemical reactivity parameters and physical properties of organic molecules using SPARC. In: Murray, J.S. (Ed.), Quantitative Treatments of Solute/Solvent Interactions. Elsevier, Amsterdam, pp. 293-353.
- Iinuma, Y., Böge, O., Gnauk, T., Hermann, H., 2004. Aerosol-chamber study of the αpinene/O₃ reaction: influence of particle acidity on aerosol yields and products. *Atmospheric Environment* 38, 761-773.
- Jang, M., Kamens, R.M., 2001. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology* 35, 4758-4766.
- Jang, M., Czoschke, N. M., Lee, S., Kamens, R. M., 2002. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* 298, 814-817.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U., 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* 12, 1659-1662.
- Liggio, J., Li, S., McLaren, R., 2005. Heterogeneous reactions of glyoxal on particulate matter: identification of acetals and sulfate esters. *Environmental Science and Technology* 39, 1532-1541.
- Limbeck, A., Kulmala, M., Puxbaum, H., 2003. Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. *Geophysical Research Letters* 30, DOI:10.1029/2003/GL017738.
- Matsunaga, S., Mochida, M., Kawamura, K., 2004. Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan. *Journal of Geophysical Research (Atmospheres)* 109, D04302/1-D04302/9.
- Mazurek, M.A., Mason-Jones, M.C., Mason-Jones, H.D., Salmon, L.G., Cass, G.R., Hallock, K.A., Leach, M., 1997. Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park 1: Properties observed by high resolution gas chromatography. *Journal of Geophysical Research* 102, 3779-3793.
- Mazurek, M.A., 2002. Molecular identification of organic compounds in atmospheric complex mixtures and relationship to atmospheric chemistry and sources. *Environmental Health Perspectives* 110, 995-1003.

- Mukai, H., Ambe, Y., 1986. Characterization of a humic-like brown substance in airborne particulate matter and tentative identification of its origin. *Atmospheric Environment* 20, 813-819.
- Pankow, J.F., 1994a. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185-188.
- Pankow, J.F., 1994b. An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* 28, 189-193.
- Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001. Properties of Gases and Liquids, 5th ed. McGraw Hill, New York, pp. 768.
- Richter, H., Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot—A review of chemical reaction pathways. *Progress in Energy and Combustion Science* 26, 565-608.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., 1993. Quantification of organic aerosols at a molecular level: identification, abundance and seasonal variability. *Atmospheric Environment* 27a, 1309-1330.
- Samburova, V., Kalberer, M., Zenobi, R., 2005. Characterization of high molecular weight compounds in urban atmospheric particles. *Atmospheric Chemistry and Physics Discussions* 5, 437-454.
- Seinfeld, J.H., Erdakos, G.B., Asher, W.E., Pankow, J.F., 2001. Modeling the formation of secondary organic aerosol. 2. The predicted effects of relative humidity on aerosol formation in the α -pinene-, β -pinene-, sabinene-, Δ^3 -carene-, and cyclohexene-ozone systems. *Environmental Science and Technology* 35, 1164-1172.
- Tobias, H.J., Ziemann, P.J., 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environmental Science and Technology* 34, 2105-2115.
- Tolocka, M.P., Jang, M., Ginter, J.M., Cox, F.J., Kamens, R.M., Johnston, M.V., 2004. Formation of oligomers in secondary organic aerosol. *Environmental Science and Technology* 38, 1428-1434.
- Zappoli, S., Andracchio, A., Fuzzi, S., Facchini., M.C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, Á., Mészáros, E., Hansson, H.C., Rosman, K., Zebühr, Y., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmospheric Environment* 33, 2733-2743.

CHAPTER 4

Thermodynamics of the Formation of Atmospheric Organic Particulate Matter by Accretion Reactions: Carboxylic and Dicarboxylic Acids

4.1 Introduction

The molecular level characterization of organic particulate matter (OPM) formed in the atmosphere has proven difficult. The complexity of such OPM is partially a result of the innumerable pathways by which organic compounds can react to form OPM. Volatile organic compounds (VOCs) can be oxidized to form multi-functional compounds; those oxidation products of sufficiently low vapor pressure can condense to form OPM. Additionally, oxidation products may undergo "accretion reactions" with one another and/or other atmospheric constituents to form products of higher-molecular weight (MW) and lower volatility, and thus increase their tendency to condense. Significant studies in this context include Haagen-Smit (1952), Tobias and Ziemann (2000), and Jang and Kamens (2001b). It has been suggested that a significant fraction of atmospheric OPM samples can be comprised of high-MW/low-volatility compounds, referred to as "oligomers" (Havers et al., 1998; Samburova et al., 2005). The presence of such compounds in the atmosphere would be consistent with accretion reactions of a variety of types (Gao et al., 2004a,b; Iinuma et al., 2004; Jang et al., 2002; Kalberer et al., 2004; Limbeck et al., 2003; Tobias and Ziemann, 2000; Tolocka et al., 2004).

Chamber studies have focused on accretion reactions as a general mechanism for OPM formation, and on the possibility of a role for acid-catalysis in increasing OPM formation by certain such reactions (e.g., Jang and Kamens, 2001b). More recently,

studies have begun to consider the detection and quantification of oligomers per se, and on the effects of particle acidity and parent compound structure. The latter chamber studies have shown that: 1) atmospherically relevant constituents, though not necessarily at atmospherically relevant levels, react to form oligomers (Gao et al., 2004a,b; Iinuma et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004); 2) a significant fraction of total OPM formed in chamber experiments can be comprised of oligomers, in some cases >50% (Gao et al., 2004a; Kalberer et al., 2004); 3) inorganic seed particles are not required for oligomer formation (Kalberer et al., 2004); when inorganic seed particles are present, the extent of oligomer formation is affected by particle acidity (Gao et al., 2004b; Iinuma et al., 2004; Jang et al., 2002; Tolocka et al., 2004); and 4) the nature of precursor aerosol seed affects the type and extent of oligomer formation (Gao et al., 2004a,b; Kalberer et al., 2004). Despite such advances, many uncertainties exist regarding accretion reactions as they may occur in the atmosphere. For example, in a chamber study involving the oxidation of α -pinene, a highly relevant biogenic OPM precursor, Tolocka et al. (2004) suggested that one of the several oligomers they detected could be explained by nine different possible combinations of monomers.

The development and application of a general theoretical approach to evaluate the thermodynamic favorabilities of accretion reactions has been discussed in Chapters 2 and 3. For C₄-C₁₀ aldehydes, ketones, dialdehydes, and diketones, and methylglyoxal, it was concluded that: 1) hydration, oligomerization, hemiacetal/acetal formation, and aldol condensation are not favored for mono- and diketones, and \sim C₅ and lower mono- and dialdehydes; 2) aldol condensation of \sim C₆ and higher mono- and dialdehydes may contribute to atmospheric OPM formation under some circumstances when kinetically favored; and 3) diol and diol-oligomer formation from glyoxal as well as aldol condensation of methylglyoxal are thermodynamically favored and may contribute significantly to OPM in the atmosphere when kinetically favored.

In this chapter, OPM formation by reaction of mono- and dicarboxylic acids to form esters and amides is considered. The study compounds are acetic, malic, maleic, and pinic acid (Figure 4.1).



Figure 4.1 Parent carboxylic and dicarboxylic acids.

Carboxylic acids are of interest because they are produced by oxidation of both anthropogenic and biogenic VOCs (Grosjean et al., 1978; Jang and Kamens, 2001a; Yu et al., 1999); ester and amide formation are among the most important reactions involving carboxylic acids (Loudon, 1995).

4.2 Theory

The proposed mechanism by which oxidation products and other atmospheric constituents A and B may contribute to OPM formation is

$$\begin{array}{ll} A_g + B_g \leftrightarrow C_g & \mbox{accretion in the gas phase, then} & (4.1) \\ C_g \leftrightarrow C_{liq} & \mbox{gas/particle equilibration of accretion product} & (4.2) \end{array}$$

in which C is a relatively high-MW/low-volatility compound. Accretion of A and B may also occur according to the following thermodynamically equivalent schemes: 1) $A_g + B_{liq} \leftrightarrow C_{liq}$, then $C_{liq} \leftrightarrow C_g$; and 2) $A_{liq} + B_{liq} \leftrightarrow C_{liq}$, then $C_{liq} \leftrightarrow C_g$. The conclusions of thermodynamic analysis (predicted extents of OPM formation) are independent of the actual scheme by which an accretion reaction proceeds and whether an acid/base catalyst is present in the OPM phase.

The thermodynamic framework used to predict OPM formation by accretion reactions has been previously described in Chapters 2 and 3. Briefly, equilibrium for an accretion reaction (e.g., as shown in Equation (4.1)) is governed by the equilibrium constant *K*, which is set by the Gibbs free energy of reaction $\Delta G^{\circ} (=\sum_{i} v_{i} \Delta G_{f,i}^{\circ})$ according to $\Delta G^{\circ} = -RT \ln K$, where: v_{i} is the stoichiometric coefficient for compound *i* in the accretion reaction; $\Delta G_{f,i}^{\circ}$ (kJ mol⁻¹) is the standard free energy of formation for *i*; *R* (8.314 x 10⁻³ kJ mol⁻¹ K⁻¹) is the ideal gas constant; and *T* (K) is temperature. Equilibrium for gas/particle (G/P) partitioning of the parent compounds and product (e.g., as shown in Equation (4.2)) is governed largely by each constituent's pure-liquid vapor pressure p_{L}° (atm), and is determined by its equilibrium G/P partitioning constant K_{p} (m³ µg⁻¹) as described by Pankow (1994b). The tendency of any given accretion reaction to form significant OPM is dependent on *K* and K_{p} , as well as the driving force for accretion product formation as provided by the initial amounts of reactants and the concentration of non-accretion related OPM into which C can initially condense, referred to here as OPM_{na} .

4.3 Mathematical Solution Process

4.3.1 Estimation of vapor pressures (p_{L}^{o}) and free energies of formation (ΔG_{f}^{o})

Needed $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ values were obtained from the literature when available. When not available, $p_{\rm L}^{\circ}$ values were estimated using SPARC (Hilal et al., 1994) and $\Delta G_{\rm f}^{\circ}$ values were estimated using the method of Benson (1976) as implemented by the CHETAH (2002) algorithm. For molecular groups not found in the CHETAH database (Table 4.1), or missing enthalpy of formation ($\Delta H_{\rm f}^{\circ}$) or entropy (S°) data, their $\Delta H_{\rm f}^{\circ}$ and S° values were estimated using linear interpolation as described by Frurip et al. (2002).

4.3.2 Mass Balance

In Section 3.3.2, it was shown that mass balance considerations lead to the following expression for initial concentration (A_0 in $\mu g m^{-3}$) of the parent compound A

$$\mathbf{A}_{0} = \mathbf{A}_{g} + \mathbf{A}_{\text{liq}} + \sum_{i=1}^{N} \left(\mathbf{C}_{i,g} \times \frac{\mathbf{v}_{A} \mathbf{M} \mathbf{W}_{A}}{\mathbf{v}_{C,i} \mathbf{M} \mathbf{W}_{C,i}} \right) + \sum_{i=1}^{N} \left(\mathbf{C}_{i,\text{liq}} \times \frac{\mathbf{v}_{A} \mathbf{M} \mathbf{W}_{A}}{\mathbf{v}_{C,i} \mathbf{M} \mathbf{W}_{C,i}} \right) \quad (4.3)$$

where we allow that A_g and A_{liq} can denote the concentrations (µg m⁻³) of A in the gas and liquid phases, as well as simply A in the gas and liquid OPM phases (see Equation (4.1)). Similarly, we allow $C_{i,g}$ and $C_{i,liq}$ to represent the gas- and liquid-phase concentrations (µg m⁻³) of the *i*th product C. The parameter *N* is the number of possible products from A. Each v is an overall stoichiometric coefficient (does not carry sign) for production of C_i from A, and each MW (g mol⁻¹) is a molecular weight. The fundamental equations describing formation of any product C_i , and G/P partitioning of A and C_i at equilibrium (Pankow, 1994a), can be used to express A_{liq} , $C_{i,g}$, and $C_{i,liq}$ in terms of A_g (see Chapter 3, Sections 3.2 and 3.3); Equation (4.3) is then easily solved for A_g given the necessary input parameters. Analogous expressions of Equation (4.3) exist for reaction schemes different from Equation (4.1).

Group: Benson Notation	Group: Physical Description	$\Delta H_{\rm f}^{\circ}~({\rm kJ~mol}^{-1})$	S° (J mol ⁻¹ K ⁻¹)
CH-(=C,0,CO)	C singly bonded to 1 H, 1 C=, 1 O, and 1 C=O	-27.5	-44.2
CH-(N,CO,C)	C singly bonded to 1 H, 1 N, 1 C=O, and 1 C	-20.9	-48.7
O-(C, CO)	O singly bonded to 1 C and 1 C=O	-179.8	12.9
CO-(=C,N)	C doubly bonded to 1 O, and singly bonded to $1 = C$ and $1 N$	-130.5	66.0
N-(3CO)	N singly bonded to 3 C=O	-127.7	-99.6

Table 4.1 Molecular groups with ΔH_{f}° and S° data unavailable in the CHETAH (2002) database and their interpolated ΔH_{f}° and S° values; carbon: C, doubly bonded carbon: C=, hydrogen: H, oxygen: O, nitrogen: N, carbonyl: C=O.

4.4 Cases

OPM formation by the Figure 4.2 accretion reactions was computed (using the standard Excel Solver, executed through a subroutine written in Visual Basic) for acetic, malic, maleic, and pinic acids with 2-methyl-3-buten-1,2-ol (MBO), diethylamine (DEA), and ammonia (NH₃). Individual accretion reactions and products are listed in Table 4.2. In Case 1, A₀ ranged from 10^{-3} - $10^3 \mu g m^{-3}$ with RH = 20%; in Case 2, A₀ = 1 $\mu g m^{-3}$ with RH from 5-95%. In both cases, it was assumed that MBO₀ and DEA₀ = 1 $\mu g m^{-3}$, NH₃ was held constant at ~0.07 $\mu g m^{-3}$ (based on a lower-limit ambient value from Seinfeld and Pandis, 2003), OPM_{na} = 10 $\mu g m^{-3}$, *P* = 1 atm, and *T* = 298 K. Values of activity coefficients in the OPM phase (ζ) were set equal to 1 (see Section 2.5.2 for discussion).

4.5 Results

4.5.1 Predicted OPM formation in Case 1; $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$, MBO₀ and DEA₀ = 1 $\ \mu g \ m^{-3}$, NH₃ = 0.07 $\ \mu g \ m^{-3}$, and RH = 20%

Figure 4.3 illustrates predicted levels of total additional OPM by the Figure 4.2 accretion reactions of acetic, malic, maleic, and pinic acids, respectively. In Chapter 3 a "criterion of importance" was established such that a compound would be of interest from a mass-based perspective (under the assumed conditions) if it could raise the OPM level by 1%. For the conditions of Case 1, when $A_0 = 1 \ \mu g \ m^{-3}$, maleic, malic, and pinic acids meet that criterion, with the levels predicted of additional OPM as follows: 1.2 (maleic), 1.2 (malic), and 0.27 (pinic) $\mu g \ m^{-3}$. For each of these acids, an ester is the dominant accretion product in the OPM phase (me.3, m.6, and p.3); however, amides (predominately 15) also contribute to total additional OPM (see Figures 4.4, 4.5, and 4.6).

For maleic and malic acids, the linear relationship between additional OPM formation and A_0 approximately along the 1:1 line (Figure 4.3) is a consequence of essentially complete conversion of the parent compound to condensable products. Extending the lower limit of A_0 would eventually resultant in a divergence of these two lines at the point where, for one or both of the acids, the driving force for product



Figure 4.2 Accretion reactions of interest for acetic, malic, maleic, and pinic acids, shown here for malic acid.

Accretion product	<i>n</i> Parent compound	<i>m</i> Alcohol or amine	Type of accretion product	Type of linkage	
<i>n</i> malic acid + <i>m</i> 2-methyl-3-butene-1,2-ol \leftrightarrow oligomer + (<i>n</i> + <i>m</i> - 1) H ₂ O					
m.1	1	1	monomer	ester	
m.2	1	2	monomer	ester	
m.3	2	1	dimer	ester	
m.4	2	2	dimer	ester	
m.5	2	3	dimer	ester	
m.6	3	2	trimer	ester	
m.7	3	3	trimer	ester	
<i>n</i> malic acid + <i>m</i> diethylamine \leftrightarrow oligomer + (<i>n</i> + <i>m</i> - 1) H ₂ O					
m.8	1	1	monomer	amide	
m.9	1	2	monomer	amide	
<i>n</i> malic acid + <i>m</i> ammonia \leftrightarrow oligomer + (<i>n</i> + <i>m</i> - 1) H ₂ O					
m.10	1	1	monomer	amide	
m.11	1	2	monomer	amide	
m.12	2	1	dimer	amide	
m.13	2	2	dimer	amide	
m.14	2	3	dimer	amide	
m.15	3	1	trimer	amide	
m.16	3	2	trimer	amide	
m.17	3	3	trimer	amide	
m.18	3	4	trimer	amide	
m.19	4	4	tetramer	amide	
Corresponding ac a.12. and a.15), n	ccretion products w naleic acid (me.1-1	vere considered for 19), and pinic acid (j	acetic acid (a.1, p.1-19). For ma	a.3, a.8, a.10, leic acid,	
formation of the hydrate (me 20) was also considered					

Table 4.2. Summary of accretion reactions and products of interest, including type of product and linkage.

formation of the hydrate (me.20) was also considered.



Figure 4.3 Predicted total additional OPM by accretion reactions of acetic, malic, maleic, and pinic acids as a function of A_0 , when $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$ (MBO₀ and DEA₀ = 1 $\ \mu g \ m^{-3}$, NH₃ = 0.07 $\ \mu g \ m^{-3}$, OPM_{na} = 10 $\ \mu g \ m^{-3}$, RH = 20%).



Figure 4.4 Fractional contribution of each of the dominant accretion products to total additional OPM as a function A_0 , when $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$ (MBO₀ and DEA₀ = 1 $\ \mu g \ m^{-3}$, NH₃ = 0.07 $\ \mu g \ m^{-3}$, OPM_{na} = 10 $\ \mu g \ m^{-3}$, RH = 20%).



Figure 4.5 Fractional contribution of each of the dominant accretion products to total additional OPM as a function A_0 , when $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$ (MBO₀ and DEA₀ = 1 $\ \mu g \ m^{-3}$, NH₃ = 0.07 $\ \mu g \ m^{-3}$, OPM_{na} = 10 $\ \mu g \ m^{-3}$, RH = 20%).



Figure 4.6 Fractional contribution of each of the dominant accretion products to total additional OPM as a function A_0 , when $A_0 = 10^{-3}$ to $10^3 \ \mu g \ m^{-3}$ (MBO₀ and DEA₀ = 1 $\ \mu g \ m^{-3}$, NH₃ = 0.07 $\ \mu g \ m^{-3}$, OPM_{na} = 10 $\ \mu g \ m^{-3}$, RH = 20%).

formation provided by A_0 is not sufficient such that all of A_0 reacts to form accretion products. While esterification and amide formation are thermodynamically favorable for acetic acid, the p_L° values of the accretion products are insufficiently low to allow significant condensation of the products. Thus, even when $A_0 = 10^3 \ \mu g \ m^{-3}$, the predicted level of additional OPM by the reactions of acetic acid is not significant ($\approx 9 \ x \ 10^{-8} \ \mu g \ m^{-3}$).

For malic, maleic, and pinic acids, as A_0 increases from 10^{-3} to $10^3 \ \mu g \ m^{-3}$, increases in total additional OPM are predicted (Figure 4.3), as well as changes in OPM composition. In the case of maleic acid, the dominant accretion product shifts from the ester me.3 to the amide me.15 (Figure 4.4); with malic acid, from the ester m.3 to the ester m.6 and then to the amide m.15 (Figure 4.5); and with pinic acid, from the amide p.8 to the ester p.3 and then to the amide p.15 (Figure 4.6). Recalling that NH₃ was held constant at a lower-limit ambient value (0.07 µg m⁻³), when we allow NH₃ to be held constant at higher values, up to 10 µg m⁻³ (within range of ambient values from Finlayson-Pitts and Pitts, 2000), the conclusions regarding significance of total additional OPM formation by reaction of each acid do not change. For acetic and pinic acids, levels of total additional OPM increase due to the increased driving force for product formation (Figure 4.7). For maleic and malic acids, predicted additional OPM decreases slightly due to the increased favorability of a less-condensable accretion product, amide 15, over the esters me.3 and m.6 (respectively). These results suggest that levels of OPM do not increase monotonically with increases in total initial concentrations of reactants. Thus, for those accretion reactions that are thermodynamically favorable in the atmosphere, ambient levels of reactants and ratios of reactants will likely affect extents of OPM formation, as well as composition.

4.5.2 Predicted OPM formation in Case 2; $A_0 = 1 \ \mu g \ m^{-3}$, MBO_0 and $DEA_0 = 1 \ \mu g \ m^{-3}$, $NH_3 = 0.07 \ \mu g \ m^{-3}$, and RH = 5% to 95%

For maleic acid, varying RH has no effect on composition or levels of total additional OPM predicted. For acetic acid, varying RH has no effect on OPM composition, but decreasing RH results in an increase in total additional OPM; however, even at the lowest RH considered, the predicted level of OPM is not significant.



Figure 4.7 Predicted levels of total additional OPM as a function NH₃ concentration (held constant), when $A_0 = 1 \ \mu g \ m^{-3}$ (MBO₀ and DEA₀ = 1 $\mu g \ m^{-3}$, OPM_{na} = 10 $\mu g \ m^{-3}$, RH = 20%).

For malic and pinic acids, varying RH affects OPM composition, and increasing RH results in decreases in the total additional OPM predicted. In the case of malic acid, even when RH = 95%, the level of OPM meets the criterion of significance; however, in the case of pinic acid, when RH > 50%, predicted levels of OPM are below the criterion of significance (when RH = 50%, OPM $\approx 6 \times 10^{-2} \,\mu g \, m^{-3}$; when RH = 95%, OPM $\approx 2 \times 10^{-2} \,\mu g \, m^{-3}$). While water is a co-product of all the dominant accretion products, only for pinic acid are the *K* values sufficiently small that the extent of accretion product formation is significantly affected by changes in RH (as RH increases, equilibrium shifts toward the reactants). For pinic acid, if we take into account the uncertainty in the necessary $\Delta G_{\rm f}^{\circ}$ values (see discussion in Section 3.5.3), adjusting the *K* values to favor accretion product formation by varying $\Delta G_{\rm f}^{\circ}$ values, then, when RH = 95 %, the predicted level of OPM meets the criterion of significance ($\approx 1 \,\mu g \, m^{-3}$). Thus, whether RH significantly affects OPM formation in the atmosphere will be case dependent. With regard to the actual levels of OPM formed via atmospheric accretion reactions, additional factors must be considered, including temperature.

The levels and composition of predicted additional OPM in Figures 4.3-4.7 are for T = 298 K. In any real environmental situation, lower temperatures are likely to be observed. For all of the accretion reactions considered, ΔH° values are negative and thus, lowering temperature favors product formation. Assuming ΔH° values are independent of temperature over a small range, for a 10°K decrease in temperature (in this case to 288 K), calculated equilibrium constants increase by ~1-4 orders of magnitude (across the range of reactions considered). In addition to increasing favorability for accretion product formation, decreasing temperature will result in lower vapor pressures of the accretion products, thereby increasing partitioning of the products to the particle phase. Therefore, from a thermodynamic perspective, decreasing temperature will favor the formation of OPM via the accretion reactions considered here.

4.5.3 Implications for observed oligomer formation in chamber studies

The chamber studies of Gao et al. (2004a,b), Iinuma et al. (2004), and Tolocka et al. (2004) involved oxidation of α -pinene, which is known to produce a number of cyclic compounds including pinic acid, hydroxy pinonaldehyde, and pinonaldehyde (Yu et al., 1999). It has been suggested that cyclic compounds can undergo ring-opening in the presence of a weak acid (Chakraborty et al., 2003; Shi and Xu, 2002; Tolocka et al., 2004). For hydroxy pinonaldehyde and pinonaldehyde there are potentially six ring-opening products (Figure 4.8); addition of water across the unsaturated bond of each product forms a total of four alcohols and two diols.

To determine whether esterification may have been important in the chamber studies of Gao et al. (2004a,b), Iinuma et al. (2004), and Tolocka et al. (2004), OPM formation was evaluated for pinic acid with the six hydrated ring-opening products (see Figure 4.8 and Table 4.3). Levels of OPM were computed for reacted α -pinene concentrations (Δ HC) ranging from ~6 to 19,000 µg m⁻³, which correspond to ~1 to 3400 ppb and were based on the range of mixing ratios used in the chamber experiments of Then, initial concentrations of pinic acid, hydroxy pinonaldehyde, and interest. pinonaldehyde were estimated based on the Δ HC values and published molar yield values reported by Yu et al., 1999. Finally, the initial concentrations of the ring-opening products were obtained by assuming all of the hydroxy pinonaldehyde and pinonaldehyde undergoes ring-opening, and schemes I and II occur with equal frequency. It was also assumed that $OPM_{na} = 0 \ \mu g \ m^{-3}$ (i.e., no organic aerosol was present in chamber initially), P = 1 atm, T = 298 K, and RH = 50% (average RH for chamber experiments). The assumed initial conditions and results of the thermodynamic analysis are summarized in Table 4.4.

For pinic acid with the hydrated ring-opening products, OPM formation by esterification is predicted with each of the Δ HC values considered. Even with the lowest Δ HC value (~ 1 ppb) the predicted level of OPM is non-negligible ($\approx 0.2 \ \mu g \ m^{-3}$). As the Δ HC values increase (and thus, the initial reactant concentrations increase), the dominant accretion products do not change; but the number of accretion products that contribute to predicted total additional OPM, and the level of predicted total additional OPM, increase.



Figure 4.8 Potential ring-opening schemes (I and II) and products of hydroxy pinonaldehyde and pinonaldehyde. Ring-opening product hpa/pa shown reacting with water to form a hydrate (hpa.20/pa.20), followed by the hydrated ring-opening product reacting with pinic acid to form an ester (hpa.21/pa.21).

Accretion Product	<i>n</i> Parent Compound	<i>m</i> H ₂ O or Alcohol/Diol	Type of Accretion Product	Type of Linkage
<i>n</i> pinic acid + m H ₂ O \leftrightarrow hydrate				
hpb.20	1	1	monomer	alcohol
<i>n</i> pinic acid + <i>m</i> alcohol/diol \leftrightarrow oligomer + (n - 1) H ₂ O				
hpb.21	1	1	monomer	ester
hpb.22	1	2	monomer	ester
hpb.23	2	1	dimer	ester
hpb.24	2	2	dimer	ester
hpb.25	2	3	dimer	ester
hpb.26	3	2	trimer	ester
hpb.27	3	3	trimer	ester

Table 4.3 Summary of accretion products, including type and linkage, for accretion reactions of pinic acid with hydrated ring-opening products of hydroxy pinonaldehyde and pinonaldehyde.

Corresponding accretion reactions and products were considered for pinic acid with the additional hydrated hydroxy pinonaldehyde ring-opening products (accretion products: hpa.20-hpa.22, hpc.20-hpc.22, and hpd.20-hpd.27) and the hydrated pinonaldehyde ring-opening products in Figure 4.8 (accretion products: pa.20-pa.22, pb.20-pb.22, pc.20-pc.22, and pd.20-pd.22).

Initial Concentration of Pinic Acid (µg m ⁻³)	Initial Concentration of Hydroxy Pinonaldehyde (µg m ⁻³)	Initial Concentration of Pinonaldehyde (µg m ⁻³)	Total additional OPM (µg m ⁻³)	Dominant Accretion Products (> 0.1% of Total Additional OPM) in Decreasing Order of Contribution
0.41	0.16	0.89	0.15	ester (hpd.23), ester (hpb.23), diester (hpb.26)
3.8	1.5	8.3	1.7	ester (hpd.23), ester (hpb.23), diester (hpb.26)
19	7.5	41	8.9	ester (hpd.23), ester (hpb.23), diester (hpb.26), ester (hpc./pc.21), ester (pb.21)
38	15	83	18	ester (hpd.23), ester (hpb.23), diester (hpb.26), ester (hpc./pc.21), ester (pb.21), ester (pd.21)
57	23	120	27	ester (hpd.23), ester (hpb.23), diester (hpb.26), ester (hpc./pc.21), ester (pb.21), ester (pd.21)
1300	500	2800	650	ester (hpd.23), ester (hpb.23), diester (hpb.26), ester (hpc./pc.21), ester (pb.21), ester (pd.21), ester (hpa./pa.21), hydrate (pb.20), hydrate (hpc./pc.20)

Table 4.4 Predicted total additional OPM by esterification of pinic acid and hydrated ring-opening products of hydroxy pinonaldehyde and pinonaldehyde. P = 1 atm, T = 298 K, RH = 50%

The molecular weights of the dominant accretion products (256 to 695 g mol⁻¹) are within the MW range of the oligomers detected in the chamber experiments of Gao et al. (2004a,b) and Iinuma et al. (2004); the functional groups of the dominant accretion products are also consistent with the functional groups observed in the chamber experiments of interest. In both the theoretical and experimental analyses, the accretion products are assumed to be combinations of low-MW monomers, though the specific accretion reactions proposed, and their products, differ. The results obtained by thermodynamic analysis suggest that esterification of pinic acid (and potentially other carboxylic/dicarboxylic acids produced via oxidation of α -pinene), with hydrated ringopening products, may have been a significant contributor to OPM formed in the chamber experiments of Gao et al. (2004a,b), Iinuma et al. (2004), and Tolocka et al. (2004).

Based on the estimation method utilized here to obtain $\Delta G_{\rm f}^{\circ}$ values, the addition of water across the unsaturated bond of the ring-opening products is thermodynamically favorable. If kinetically favorable, other cyclic oxidation products may form alcohols/diols in the same way as α -pinene. Unsaturated oxidation products, similar to the ring-opening products of hydroxy pinonaldehyde and pinonaldehyde, may also undergo hydration to form alcohols/diols. Given the numerous generation possibilities for reactants, esterification reactions may be important in chamber experiments involving oxidation of VOCs other than α -pinene, including those of Gao et al. (2004a,b).

4.6 References

Benson, S.W., 1976. Thermochemical Kinetics. Wiley, New York, pp. 336.

- Chakraborty, D., Rodriguez, A., Chen, E.Y.-X., 2003. Catalytic ring-opening polymerization of propylene oxide by organoborane and aluminum Lewis acids. *Macromolecules* 26, 5470-5481.
- CHETAH Version 7.3: The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (CHETAH), 2002. ASTM International, Pennsylvania.
- Finlayson-Pitts, B.J, Pitts, J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, California, pp. 969.
- Gao, S., Keywood, M., Ng, N.L., Surratt, J., Varutbangkul, R.B., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004a. Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α-pinene. *Journal of Physical Chemistry A* 108, 10147-10164.
- Gao, S., Ng, N.L., Keywood, M., Varutbangkul, R.B., Bahreini, R., Nenes, A., He, J., Yoo, K.Y., Beauchamp, J.L., Hodyss, R.P., Flagan, R.C, Seinfeld, J.H., 2004b. Particle phase acidity and oligomer formation in secondary organic aerosol. *Environmental Science and Technology* 38, 6582-6589.
- Grosjean, D., Van Cauwenberghe, K., Schmid, J.P., Kelley, P.E., Pitts, J.N., 1978. Identification of C3-C10 aliphatic dicarboxylic acids in airborne particulate matter. *Environmental Science and Technology* 12, 313-317.
- Haagen-Smit, A.J., 1952. Chemistry and physiology of Los Angeles smog. *Industrial Engineering and Chemistry* 44, 1342-1346.
- Havers, N., Burpa, P., Lambert, J., Klockow, D., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *Journal of Atmospheric Chemistry* 29, 45-54.
- Hilal, S.H., Carreira, L.A., Karickhoff, S.W., 1994. Estimation of chemical reactivity parameters and physical properties of organic molecules using SPARC. In: Murray, J.S. (Ed.), Quantitative Treatments of Solute/Solvent Interactions. Elsevier, Amsterdam, pp. 293-353.
- Iinuma, Y., Böge, O., Gnauk, T., Hermann, H., 2004. Aerosol-chamber study of the αpinene/O₃ reaction: influence of particle acidity on aerosol yields and products. *Atmospheric Environment* 38, 761-773.

- Jang, M., Kamens, R.M., 2001b. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology* 35, 4758-4766.
- Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* 298, 814-817.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U., 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* 12, 1659-1662.
- Loudon, M.G., 1995. Organic Chemistry, 3rd ed. Benjamin/Publishing Company, California, pp. 1390.
- Limbeck, A., Kulmala, M., Puxbaum, H., 2003. Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. *Geophysical Research Letters* 30, DOI:10.1029/2003/GL017738.
- Pankow, J.F., 1994a. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185-188.
- Pankow, J.F., 1994b. An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* 28, 189-193.
- Samburova, V., Kalberer, M., Zenobi, R., 2005. Characterization of high molecular weight compounds in urban atmospheric particles. *Atmospheric Chemistry and Physics Discussions* 5, 437-454.
- Seinfeld, J.H, Pandis, S.N., 1998. From Air Pollution to Climate Change. John Wiley and Sons, New York, pp. 1325.
- Shi, M., Xu., B., 2002. Lewis acid-catalyzed ring-opening reactions of methylenecyclopropanes with alcoholic or acidic nucleophiles. *Organic Letters* 13, 2145-2148.
- Tobias, H.J., Ziemann, P.J., 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environmental Science and Technology* 34, 2105-2115.

- Tolocka, M.P., Jang, M., Ginter, J.M., Cox, F.J., Kamens, R.M., Johnston, M.V., 2004. Formation of oligomers in secondary organic aerosol. *Environmental Science and Technology* 38, 1428-1434.
- Yu, J., Cocker, D.R., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1999. Gas-phase oxidation products of monoterpenes: gaseous and particulate products. *Journal* of Atmospheric Chemistry 34, 207-258.

CHAPTER 5

Thermodynamics of the Formation of Atmospheric Organic Particulate Matter by Accretion Reactions: General Theoretical Framework

5.1 Introduction

The term "accretion reactions" has been used to describe the large collection of reactions by which oxidation products of volatile organic compounds can react with one another and/or other atmospheric constituents, forming products of higher-molecular weight (MW) and lower volatility, and thus increasing their tendency to condense (Barsanti and Pankow, 2004, 2005). Studies have shown that a significant fraction of atmospheric organic particulate matter (OPM) can be comprised of high-MW/low-volatility compounds (e.g., Havers et al., 1998, Samburova et al., 2005), which would be consistent with the occurrence of such accretion reactions in the atmosphere (e.g., Jang et al., 2002). However, many uncertainties exist regarding accretion reactions as they may occur in the atmosphere, including identification of those reactions most likely to contribute to OPM formation.

A general theoretical approach has been developed and applied to evaluate the thermodynamic favorabilities of accretion reactions, including the extents to which they may be relevant for OPM formation in the atmosphere. This approach requires pureliquid vapor pressure (p_L°) and Gibbs free energy of formation (ΔG_f°) values for each reactant and product of interest. For reactants and accretion products of interest in the atmosphere, few physical property data are available. Thus, group contribution methods (GCMs) have been used to estimate physical property data that are not available in the literature. Such methods are recommended based on their relative accuracies and computational efficiencies; however, they are not completely reliable (e.g., Poling et al., 2001).

In considerations of OPM formation by individual accretion reactions (see Chapters 2-4), SPARC (Hilal et al., 1994) was used to estimate needed $p_{\rm L}^{\circ}$ values and the Joback method (Reid et al., 1987) or the Benson method (1976) was used to estimate needed $\Delta G_{\rm f}^{\circ}$ values. Based on the general theoretical approach employed, including those GCMs used to estimate needed $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ values, it was concluded that: 1) hydration, oligomerization, hemiacetal/acetal formation, and aldol condensation are not favored for mono- and diketones, and $\sim C_5$ and lower mono- and dialdehydes; 2) aldol condensation of ~C₆ and higher mono- and dialdehydes may contribute to atmospheric OPM formation under some circumstances (aldol condensation of those compounds can not be ruled out due to the uncertainty in needed $\Delta G_{\rm f}^{\circ}$ values); 3) diol and diol-oligomer formation from glyoxal, as well as aldol condensation of methylglyoxal, are thermodynamically favored and may contribute significantly to OPM in the atmosphere; and 4) ester and amide formation from malic, maleic, pinic, and similar mono- and dicarboxylic acids, may contribute to atmospheric OPM when kinetically favorable. That uncertainty in $\Delta G_{\rm f}^{\circ}$ values precludes determination of whether a given accretion reaction may contribute to OPM formation in some cases, emphasizes the need to consider the level of accuracy of free energy data obtained from physical property estimation and/or experimental methods.

The theoretical method developed in Chapter 2 has been extended in this work to allow evaluation of the extent to which any type of accretion reaction may contribute to OPM formation in the atmosphere. This work builds on previous considerations of OPM formation by accretion reactions in which predictions were made using estimated $\Delta G_{\rm f}^{\circ}$ values to calculate equilibrium constants (*K*) for each accretion reaction of potential interest. In this work, levels of OPM were computed for a range of *K* values. This approach yielded a series of curves from which, given any accretion-product *K* value, initial reactant concentration, and background OPM level, the predicted level of OPM can be easily determined. This approach will allow for evaluation of atmospheric OPM formation by any type of accretion reaction of interest, assuming a knowledge of the underlying thermodynamics.

5.2 Mathematical Solution Process

5.2.1 Mass Balance

In Section 3.3.2 it was shown that mass balance considerations lead to the following expression for initial concentration (A_0 in μ g m⁻³) of the parent compound A, for an accretion reaction of the general form A + B = C,

$$A_{0} = A_{g} + A_{liq} + \sum_{i=1}^{N} \left(C_{i,g} \times \frac{\nu_{A} M W_{A}}{\nu_{C,i} M W_{C,i}} \right) + \sum_{i=1}^{N} \left(C_{i,liq} \times \frac{\nu_{A} M W_{A}}{\nu_{C,i} M W_{C,i}} \right)$$
(5.1)

where A_g and A_{liq} can denote the concentrations ($\mu g m^{-3}$) of A in the gas and liquid phases; similarly, we allow $C_{i,g}$ and $C_{i,liq}$ to represent the gas- and liquid-phase concentrations ($\mu g m^{-3}$) of the *i*th product C. The parameter *N* is the number of possible products from A. Each v is an overall stoichiometric coefficient (does not carry sign) for production of C_i from A, and each MW (g mol⁻¹) is a molecular weight. Analogs of Equation (5.1) exist for reaction stoichiometries different from A + B = C. The fundamental equations describing formation of any product C_i , and gas/particle (G/P) partitioning of A and C_i at equilibrium (Pankow, 1994), are used to express A_{liq} , $C_{i,g}$, and $C_{i,liq}$ in terms of A_g , and require ΔG_f° and p_L° values for each of the reactants and products of interest. Equation (5.1) is then easily solved for A_g given the necessary input parameters.

5.2.2 Determination of vapor pressures (p_1°) and free energies of formation (ΔG_f°)

For the reactants of interest here, $p_{\rm L}^{\circ}$ values were obtained using a five-parameter Antoine parameterization with coefficients from Yaws (1999), a three-parameter Antoine parameterization with coefficients from Bridgeman and Aldrich (1964) and Stull (1947), online material safety data sheets (Sigma-Aldrich, 2005), or estimated using the group contribution method SPARC (Hilal et al., 1994). For the general accretion products of interest, each C_i from A, p_L^o values were estimated from $p_{L,A}^o$ following the approximation that p_L^o values decrease by approximately half an order of magnitude for every carbon added. From these initially determined p_L^o values, a range of p_L^o values was assigned for each C_i . Differing from previous considerations in which ΔG_f^o values were used to calculate *K* values for each accretion reaction of interest, in this work, a range of *K* values (10⁻¹ to 10²⁰) was assumed for each accretion reaction.

5.3 Cases

Levels of OPM were predicted for general accretion reactions of the following stoichiometries: 2A = C, $2A = C + H_2O$, $A + B = C + H_2O$, and $A + 2B = C + 2H_2O$. It was assumed that the initial concentration of each reactant (A_0 and B_0) was 10 µg m⁻³ and OPM_{na}, the level of background OPM that is non-accretion related, was 10 µg m⁻³; in addition, P = 1 atm, T = 298 K, and relative humidity (RH) = 50%. As in previous considerations, the modeling assumed that little water was present in the OPM phase (consistent with the results of Seinfeld et al., 2001) and activity coefficients (ζ) ≈ 1 for all products in the OPM phase (for further discussion see Section 2.5.2).

5.4 Results and Discussion

5.4.1 Predicted additional OPM as a function of log K and p_L° ; $A_0 = 10 \,\mu g \, m^{-3}$, $OPM_{na} = 10 \,\mu g \, m^{-3}$, RH = 50%

In Figures 5.1-5.9, for each accretion product C_i the predicted level of additional OPM is shown as a function of log *K* and $p_{L,C}^o$. In all cases, it can be seen that the relationship between log *K* and OPM formation by C is nonlinear. For the accretion reactions 2A = C, Figures 5.1 (A = butanal) and 5.2 (A = hexanal), and $2A = C + H_2O$, Figures 5.3 (A = butanal) and 5.4 (A = hexanal), predicted OPM formation by C is initially controlled by log *K* and $p_{L,C}^o$, until the value of *K* is sufficiently large that p_L^o becomes the limiting factor in converting A to C_{liq} . Using the mass-based "criterion of importance" established in Chapter 3,



Figure 5.1 Predicted additional OPM formation as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 µg m⁻³ of butanal, RH = 50%, T = 298 K.



Figure 5.2 Predicted additional OPM formation as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 µg m⁻³ of hexanal, RH = 50%, T = 298 K.



Figure 5.3 Predicted additional OPM formation as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 µg m⁻³ of butanal, RH = 50%, T = 298 K.


Figure 5.4 Predicted additional OPM formation as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 µg m⁻³ of hexanal, RH = 50%, T = 298 K.

that a compound would be of interest (under the assumed conditions) if it could raise the OPM level by 1%, only for hexanal does predicted OPM formation by C reach the level of significance (when $p_{L,C}^{\circ} < 10^{-6}$). In the case of butanal, the $p_{L,C}^{\circ}$ values are insufficiently low to allow significant condensation of C.

For the accretion reaction $A + NH_3 = C + H_2O$ in Figures 5.5 (A = butanal), 5.6 (A = hexanal), and 5.7 (A = pinic acid), only for pinic acid does predicted OPM formation reach the level of significance (for all $p_{L,C}^{\circ}$ considered). In the cases of butanal and hexanal (Figures 5.4 and 5.5), for all values of *K* significant OPM formation is limited by $p_{L,C}^{\circ}$. The convergence of lines in Figure 5.7, for $10^{-12} \le p_{L,C}^{\circ} \le 10^{-10}$, is a consequence of complete conversion of pinic acid to C_{Iiq} ; the lines diverge at the lower limits of *K* where predicted OPM formation is controlled by both *K* and $p_{L,C}^{\circ}$. The same trend is observed for the general accretion reactions $A + B = C + H_2O$ and $A + 2B = C + 2H_2O$, shown in Figures 5.8 and 5.9 respectively, where A = pinic acid and B = isopropanol.

When using the series of curves generated in Figures 5.1-5.9 to determine the predicted level of OPM for a specific accretion reaction, for those accretion reactions in which $p_{\rm L,C}^{\circ}$ values do not allow for significant condensation of C, uncertainty in needed $\Delta G_{\rm f}^{\circ}$ values will not affect conclusions regarding potential relevance for atmospheric OPM formation. For all other reactions, the level of accuracy required for estimated $\Delta G_{\rm f}^{\circ}$ values (and potentially for estimated $p_{\rm L}^{\circ}$ values) will depend on both the values of *K* and of $p_{\rm L}^{\circ}$.

5.4.2 Evaluation of OPM formation by individual accretion reactions including uncertainty in estimated ΔG_{f}° values

From the series of curves generated in Figures 5.1-5.9, predicted OPM formation by specific accretion reactions can be determined, assuming a knowledge of $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ for each reactant and product of interest. The series of curves in Figures 5.5-5.8 are for an accretion reaction with the stoichiometry A + B = C + H₂O.



Figure 5.5 Predicted OPM formation by C as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 μ g m⁻³ of butanal, RH = 50%, T = 298 K.



Figure 5.6 Predicted OPM formation by C as a function of log *K* and $p_{L,C}^{o}$, when A₀ = 10 μ g m⁻³ of hexanal, RH = 50%, T = 298 K.



Figure 5.7 Predicted OPM formation by C as a function of log *K* and $p_{L,C}^{\circ}$, when A₀ = 10 μ g m⁻³ of pinic acid, RH = 50%, T = 298 K.



Figure 5.8 Predicted OPM formation by C as a function of log *K* and $p_{L,C}^{\circ}$, when $A_0 = 10 \ \mu g \ m^{-3}$ of pinic acid, $B_0 = 10 \ \mu g \ m^{-3}$ of isopropanol, RH = 50%, T = 298 K.



Figure 5.9 Predicted OPM formation by C as a function of log *K* and $p_{L,C}^{\circ}$, when $A_0 = 10 \ \mu g \ m^{-3}$ of pinic acid, $B_0 = 10 \ \mu g \ m^{-3}$ of isopropanol, RH = 50%, T = 298 K

This stoichiometry corresponds with imine (when A = carbonyl and B = amine, Figures 5.5 and 5.6), amide (A = carboxylic acid and B = amine, Figure 5.7), and ester (A = carboxylic acid and B = alcohol, Figures 5.8 and 5.9) formation. Since predicted levels of OPM in Figures 5.5 and 5.6 are not significant for any value of *K*, imine formation by butanal and hexanal with NH₃ will not be considered further.

The series of curves in Figures 5.7-5.9 were used to evaluate amide and ester formation by pinic acid, including the extent to which such accretion reactions may contribute to atmospheric OPM formation. NH₃ and isopropanol were chosen as the amine and alcohol for their atmospheric relevance. For the accretion products shown in Figure 5.10, SPARC (Hilal et al., 1994) was used to estimate $p_{\rm L}^{\circ}$ values and the method of Benson (1976) implemented by the CHETAH (2002) algorithm was used to estimate $\Delta G_{\rm f}^{\circ}$ values. Those values, and computed ΔG° and *K* values, are shown in Table 5.1. Error bounds for *K* values were computed by varying $\Delta G_{\rm f}^{\circ}$ of pinic acid by +3% and the accretion products by -3%, and vice versa ($\Delta G_{\rm f}^{\circ}$ values of water, NH₃, and isopropanol are known). The uncertainty in $\Delta G_{\rm f}^{\circ}$ values of 27 organic compounds. While the range of approximated $p_{\rm L,C}^{\circ}$ values for which levels of predicted OPM are plotted in Figures 5.7-5.9 do not necessarily encompass the estimated $p_{\rm L,C}^{\circ}$ values for the specific accretion products considered, an evaluation of OPM formation still can be made using the existing curves.

Using the values in Table 5.1 for amide formation ($p_{L,C}^{\circ} \approx 10^{-11}$, log $K \approx 1$) and the series of curves in Figure 5.7, predicted OPM formation from pinic acid and NH₃, with the reaction stoichiometry A + B = C + H₂O, does not appear to be significant. However, when the uncertainty in estimated ΔG_{f}° values is taken into account, such that log $K \approx 6$, predicted OPM meets the criterion of significance. Similarly, using the values for formation of an ester ($p_{L,C}^{\circ} \approx 10^{-9}$, log $K \approx 3$) and diester ($p_{L,C}^{\circ} \approx 10^{-7}$, log $K \approx 7$), and the series of curves in Figures 5.8 and 5.9, predicted OPM formation from pinic acid and isopropanol, with the reaction stoichiometries A + B = C + H₂O and A + 2B = C + 2H₂O,



Figure 5.10 Amide and ester formation from pinic acid.

) K			
Compound	$\log p_{\rm L}^{\circ}$ (atm)	$\frac{\Delta G_{\rm f}^{\circ}}{\rm (kJ\ mol^{-1})}$	$\frac{\Delta G^{\circ}}{(\text{kJ mol}^{-1})}$	$\frac{\log K}{(\Delta G_{\rm f}^\circ \pm 3\%)}$
water	-1.5 ^a	-228.60 ^d		
NH ₃	1.0 ^b	-16.44 ^d		
isopropanol	-1.2 °	-173.72 ^d		
pinic acid	-10.7	-561.19		
amide	-10.6	-573.30	-6.34	1 ± 5
ester	-8.5	-525.94	-19.64	3 ± 6
diester	-6.2	-492.41	-40.99	7 ± 5

Table 5.1 Reported and estimated $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ values for water, ammonia, pinic acid, and three general accretion products (an amide, an ester, and a disaster); calculated ΔG° and K values for accretion product formation from pinic acid. P = 1atm and T = 298 K

^a Bridgeman and Aldrich (1964) ^b Stull (1947)

^c Sigma-Aldrich (2005) ^d Yaws (1999)

does not appear to be significant. Taking into account uncertainty in estimated $\Delta G_{\rm f}^{\circ}$ values, such that log $K \approx 9$ for ester formation and log $K \approx 12$ for diester formation, the predicted levels of OPM are significant. These results are consistent with those reported in Chapter 4, Section 4.5.2, in which the predicted level of OPM for amide and ester formation by pinic acid was not significant when RH > 50%; when uncertainty in $\Delta G_{\rm f}^{\circ}$ values was taken into account by adjusting *K* values for each accretion reaction of interest, the predicted level OPM met the criterion of significance. It was concluded in Chapter 4 that whether RH significantly affects OPM formation in the atmosphere will be case dependent and that with regard to the actual levels of OPM formed via atmospheric accretion reactions, additional factors must be considered, including temperature. The same conclusions apply here.

For the accretion reactions considered here, amide formation with NH₃ and ester formation with isopropanol, OPM formation by pinic acid can not be ruled out under the assumed conditions. The potential contribution of those accretion reactions to atmospheric OPM formation remains uncertain, requiring further refinement in estimated $\Delta G_{\rm f}^{\circ}$ values. The series of curves in Figures 5.7-5.9 can be used to reevaluate OPM formation when higher accuracy physical property data from improved estimation and/or experimental methods becomes available.

5.5 References

- Barsanti, K.B., Pankow, J.F., 2004. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 1: Aldehydes and ketones. *Atmospheric Environment* 38, 4371-4382.
- Barsanti, K.B., Pankow, J.F., 2005. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 2: Dialdehydes, methylglyoxal, and diketones. *Atmospheric Environment* 39, 6597-6607.
- Benson, S.W., 1976. Thermochemical Kinetics. Wiley, New York, pp. 336.
- Bridgman, O.C., Aldrich, E.W., 1964. In NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov, viewed: January, 2006).
- CHETAH Version 7.3: The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (CHETAH), 2002. ASTM International, Pennsylvania.
- Havers, N., Burpa, P., Lambert, J., Klockow, D., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *Journal of Atmospheric Chemistry* 29, 45-54.
- Hilal, S.H., Carreira, L.A., Karickhoff, S.W., 1994. Estimation of chemical reactivity parameters and physical properties of organic molecules using SPARC. In: Murray, J.S. (Ed.), Quantitative Treatments of Solute/Solvent Interactions. Elsevier, Amsterdam, pp. 293-353.
- Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* 298, 814-817.
- Pankow, J.F., 1994. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185-188.
- Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001. Properties of Gases and Liquids, 5th ed. McGraw Hill, New York, pp. 768.
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. Properties of Gases and Liquids, 4th ed. McGraw-Hill, New York, pp. 741.
- Samburova, V., Kalberer, M., Zenobi, R., 2005. Characterization of high molecular weight compounds in urban atmospheric particles. *Atmospheric Chemistry and Physics Discussions* 5, 437-454.

- Seinfeld, J.H., Erdakos, G.B., Asher, W.E., Pankow, J.F., 2001. Modeling the formation of secondary organic aerosol. 2. The predicted effects of relative humidity on aerosol formation in the α -pinene-, β -pinene-, sabinene-, Δ^3 -carene-, and cyclohexene-ozone systems. *Environmental Science and Technology* 35, 1164-1172.
- Sigma-Aldrich, 2005. Product detail, 2-propanol. (http://www.sigmaaldrich.com/ catalog/search/ProductDetail/SIGMA/I9516, viewed: January, 2006).
- Stull, D.R., 1947. In NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov viewed: June, 2003).
- Yaws, C.L., 1999. Chemical Properties Handbook. McGraw-Hill, New York, pp. 600.

CHAPTER 6

Conclusions

6.1 Results Summary

6.1.1 OPM formation by accretion reactions of aldehydes and dialdehydes

In Chapter 2 a general theoretical method was developed to evaluate the thermodynamic favorabilities of accretion reactions, including the extent to which they may contribute to organic particulate matter (OPM) formation in the atmosphere. That approach was applied to evaluate OPM formation by accretion reactions of C₁₀ and lower aldehydes and ketones, with the method of Joback (as described by Reid et al., 1987) employed to estimate needed free energy of formation ($\Delta G_{\rm f}^{\circ}$) values and hence, equilibrium constant (*K*) values. Regarding OPM formation do not appear to be thermodynamically favored either in the atmosphere, or in the "acid-catalyzed" chamber experiments of Jang and Kamens (2001). Regarding the latter, the mechanism for any observed OPM formation remains unknown; whether the consequences of aldol condensation were observed remains uncertain due in part to uncertainties in the $\Delta G_{\rm f}^{\circ}$ values is required to clarify the potential importance of aldol products of pinonaldehyde in the formation of atmospheric OPM.

6.1.2 OPM formation by accretion reactions of dialdehydes and diketones

In Chapter 3, the general theoretical approach developed in Chapter 2 was applied to evaluate OPM formation by accretion reactions of C_{10} and lower dialdehydes and diketones, with the method of Benson (1976) used to predict ΔG° values and hence *K* values. For 1,4-butanedial, 2,3-butanedione, and 2,5-hexanedione, it was concluded that hydration, oligomerization, hemiacetal/acetal formation, and aldol condensation are not thermodynamically favored under the assumed conditions. For $\sim C_6$ and higher dialdehydes, reaction by aldol condensation may contribute to atmospheric OPM formation under certain circumstances, if kinetically favorable. For glyoxal, diol and subsequent oligomer formation, and for methylglyoxal, aldol condensation, are thermodynamically favorable and may contribute significantly to OPM in the atmosphere, if kinetically favorable. The actual contribution of glyoxal and methylglyoxal to atmospheric OPM will depend on the kinetics of those accretion reactions in the atmosphere.

6.1.3 OPM formation by accretion reactions of carboxylic and dicarboxylic acids

In Chapter 4, the general theoretical approach developed in Chapter 2 was applied to evaluate OPM formation by carboxylic and dicarboxylic acids via ester and amide formation. That approach, including the method used to predict $\Delta G_{\rm f}^{\circ}$ values (Benson, 1976) and therefore *K* values, indicates that for all acids considered, ester and amide formation are thermodynamically favorable under the assumed conditions. In the case of malic, maleic, and pinic acids, the accretion products have sufficiently low vapor pressures ($p_{\rm L}^{\circ}$) that they are predicted to reside predominately in the OPM phase, contributing to total OPM. Thus, for malic, maleic, and pinic acids, and likely for similar mono- and dicarboxylic acids, significant OPM formation may occur via ester and amide formation in the atmosphere when kinetically favorable.

6.1.4 OPM formation by general accretion reactions

In Chapter 5, using the general theoretical approach developed in Chapter 2, levels of OPM were computed for general accretion reactions using a range of K and $p_{\rm L,C}^{\circ}$ values. This approach yielded a series of curves from which the predicted level of OPM can be easily determined for any accretion, assuming a knowledge of $\Delta G_{\rm f}^{\circ}$ and $p_{L,C}^{\circ}$. For general accretion reactions of the stoichiometries 2A = C and $2A = C + H_2O$, where A = butanal or hexanal, only for hexanal does predicted OPM formation by C reach a level of significance. For general accretion reactions of the stoichiometries A + B $= C + H_2O$ and $A + 2B = C + 2H_2O$, where A = butanal, hexanal, or pinic acid, only for pinic acid does predicted OPM reach a level of significance. In consideration of specific accretion reactions, it was concluded that OPM formation by accretion reactions of pinic acid (specifically amide and ester formation according to the reactions stoichiometries above) can not be ruled out under the assumed conditions and their potential contribution to atmospheric OPM formation remains uncertain, requiring refinement in needed $\Delta G_{\rm f}^{\circ}$ values. This approach will allow evaluation of the potential contribution of any type of accretion reaction to atmospheric OPM formation, assuming a .knowledge of the underlying thermodynamics.

6.2 Implications for Organic Aerosol Modeling

The composition of atmospheric aerosols affects their hygroscopicity, ability to act as cloud condensation nuclei, optical properties, and role in climate forcing. Therefore, models that accurately represent the organic component of atmospheric aerosols are needed. A recent review paper by Kanakidou et al. (2005) addressing organic aerosols and global climate modeling, outlined a number of specific areas in which further research is needed. Among those relevant to the composition of OPM was the complete characterization of OPM formation in-situ, including understanding the role of oligomers.

Though OPM formation via accretion reactions has been observed in chamber studies and advanced as an explanation for the presence of high-molecular weight (MW) constituents (or "oligomers") in atmospheric OPM samples (e.g., Kalberer et al., 2004), many uncertainties exist regarding the occurrence of such reactions in the atmosphere, including identification of those reactions most likely to contribute to atmospheric OPM formation. The general theoretical approach described herein provides a method for identifying accretion reactions that may have a role in the formation high-MW compounds in the atmosphere and thus contribute to atmospheric OPM, provided that uncertainties in input variables such as $p_{\rm L}^{\circ}$ and $\Delta G_{\rm f}^{\circ}$ are considered. The thermodynamic analysis presented is not intended to provide an estimate of the actual level of OPM formed by any given accretion reaction, but rather to provide an estimate of the probability and extent to which a given accretion reaction may contribute to OPM. With regard to the actual levels of OPM formed via atmospheric accretion reactions, the general theoretical approach described could be modified and integrated into an existing organic aerosol model.

In addition to uncertainties regarding the formation of accretion products in the atmosphere, uncertainties exist as to the role of oxidation in limiting or reversing accretion product formation. Studies have shown that aliphatic compounds (assembled in films or monolayers) are subject to oxidation by hydroxyl radicals (Eliason et al., 2004; Molina et al., 2004), and that volatilization may be an important loss mechanism depending on the chemical composition of organic aerosols (Molina et al., 2004). Thus, considering the potential loss mechanisms for accretion products in the atmosphere, as well as their formation pathways, is necessary for evaluating the potential contribution of accretion reactions to atmospheric OPM and ultimately for understanding the composition of organic aerosols and their formation in-situ. Addressing these uncertainties will lead to more accurate representation of organic aerosols in regional and global models, which will in turn lead to a better understanding of the impact of organic aerosols on air quality and climate.

Benson, S.W., 1976. Thermochemical Kinetics. Wiley, New York, pp. 336.

- Eliason, T.L., Gilman, J.B., Vaida, V., 2004. Oxidation of organic films relevant to atmospheric aerosols. *Atmospheric Environment* 38, 1367-1378.
- Jang, M., Kamens, R.M., 2001. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology* 35, 4758-4766.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U., 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* 12, 1659-1662.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modeling: a review. *Atmospheric Chemistry and Physics* 5, 1053-1123.
- Molina, M.J., Ivanov, A.V., Trakhtenberg, S., Molina, L.T., 2004. Atmospheric evolution of organic aerosol. *Geophysical Research Letters* 31, DOI:10.1029/2004GL020910
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. Properties of Gases and Liquids, 4th ed. McGraw-Hill, New York, pp. 741.

APPENDIX 1

Data Extraction from Table 2 of Jang and Kamens (2001)*

Clarified definitions of the parameters utilized by Jang and Kamens (2001) are provided in Table A1.1. When expressed in terms of the symbols used in this work, the specialized definition of "yield (%)" used in Table 2 of Jang and Kamens (2001) is

"yield (%)" =
$$(v_{\text{OPM}}/V_{\text{inj}}) \times 100\%$$
 (A1.1)

for which Jang and Kamens (2001b) state

$$v_{\rm OPM} = v_{\rm TPM} - v_{\rm seed} \times 0.769 \tag{A1.2}$$

Jang and Kamens (2001) report that the factor 0.769 is a correction for a change in air volume after addition of the n-aldehyde and 1-decanol into the experimental volume.

The $n_{i,0}$ values in each of the four cases of interest were calculated based on: 1) V_{inj} values reported by Jang and Kamens (2001) (see Table A1.2) for *n*-aldehyde/1-decanol systems in the presence of a non-acidic seed aerosol; and 2) assumed *n*-aldehyde/1-decanol volume ratios of 2.5 for the butanal case and 1.0 for the hexanal, octanal, and decanal cases. The n_{na} values in each of the four cases were based on v_{OPM} values measured using non-acidic seed aerosol (see Table A1.2).

*Jang, M., Kamens, R.M., 2001. Environmental Science and Technology 35, 4758-4766.

	This Work	Jang and Kamens (2001) ^a
$V_{\rm inj}~(\mu L~{ m m}^{-3})$	= total (aldehyde + decanol) injected liquid organic volume per m ³ of chamber	= "gas concentration" and also "injected liquid organic volume"
$v_{\rm OPM} ({\rm nm}^3 {\rm cm}^{-3})$	= volume concentration of OPM	= "organic aerosol volume"
$v_{\text{TPM}} (\text{nm}^3 \text{cm}^{-3})$	= total PM volume concentration	= "particle volume" and also "aerosol volume"
$v_{\text{seed}} (\text{nm}^3 \text{ cm}^{-3})$	= seed volume concentration	= "seed volume"
$\Delta OPM (\mu g m^{-3})$		= (OPM reported with acidic-seed aerosol) - (OPM reported with non-acidic seed aerosol)

Table A1.1 Definitions of parameters used in data extraction from Jang and Kamens (2001).

^a Jang, M., Kamens, R.M., 2001. Environmental Science and Technology 35, 4758-4766.

Parent Aldehyde	$V_{\rm inj}$ (µL m ⁻³)	$\frac{v_{\text{TPM}}}{(\text{nm}^3 \text{ cm}^{-3})}$	$(\text{nm}^3 \text{ cm}^{-3})$	$(\text{nm}^3 \text{ cm}^{-3})$	<i>n</i> _{na} (mols)
<i>n</i> -butanal	50	3.70 x 10 ¹⁰	2.53 x 10 ⁹	3.51 x 10 ¹⁰	8.76 x 10 ⁻⁸
<i>n</i> -hexanal	17	3.84 x 10 ¹⁰	4.14 x 10 ¹⁰	6.56 x 10 ⁹	1.64 x 10 ⁻⁸
<i>n</i> -octanal	17	2.13 x 10 ¹¹	1.68 x 10 ¹⁰	$2.00 \ge 10^{11}$	5.00 x 10 ⁻⁷
<i>n</i> -decanal	17	2.14 x 10 ¹¹	1.57 x 10 ¹⁰	$2.02 \ge 10^{11}$	5.00 x 10 ⁻⁷

Table A1.2 Data extracted from selected chamber experiments of Jang and Kamens (2001)^a conducted at T = 298 K in the presence of a non-acidic seed aerosol.

^a Jang, M., Kamens, R.M., 2001. Environmental Science and Technology 35, 4758-4766.

APPENDIX 2

Known Polymerization Behavior of Aldehydes and Ketones

In solution, except for formaldehyde and carbonyls with highly electronegative groups, the reaction equilibrium between a simple carbonyl and its hydrate does not favor the hydrate (Dean, 1987*; Loudon, 1995**). Hemiacetal formation by reaction of an aldehyde with an alcohol is similarly not favored (Dean, 1987); acetal formation is not favored unless the solution is very dry (Dean, 1987). Ketones tend to undergo hydration and acetal formation less readily than their analogous aldehydes (Loudon, 1995). The estimated log K values for hydration and hemiacetal formation in solution given in Table A2.1 predict equilibrium positions that are qualitatively in good agreement with these Estimated log K values for acetal formation and α,β -unsaturated reported trends. carbonyl formation in solution are given in Table A2.2. When the initial parent carbonyl mole fraction in solution $X_{carbonvl} = 0.9$, the aldol condensation equilibrium favors formation of the α,β -unsaturated carbonyl from both aldehydes and ketones, even when the solution is not dry (Dean, 1987; Loudon, 1995). For Cases 1-4, the liquid phase mole fractions that would correspond to the initial gaseous pressures of n-butanal, n-hexanal, *n*-octanal, and *n*-decanal are given by $X_{\text{carbonyl}} \approx p/p_{\text{L}}^{\circ}$, and equal 6×10^{-5} , 1×10^{-4} , 9×10^{-4} , and 8×10^{-3} , respectively. It is the fact that these values are so much lower than 0.9 that is responsible for the greatly lower importance of the aldol products in those cases.

^{*}Dean, J.A. 1987. Handbook of Organic Chemistry. McGraw-Hill, New York. **Loudon, Mark G., 1995. Organic Chemistry, 3rd ed. Benjamin/Publishing Company, California.

Hydrate Formation ^a			Hemiacetal Formation ^b		
Carbonyl + Water = Hydrate		Carbonyl + Alcohol = Hemiacetal			
Parent Carbonyl	Log K _{hydrate}	$\frac{X_{\text{hydrate}}}{X_{\text{carbonyl}}}$	Parent Carbonyl	Log $K_{ m hemiacetal}$	$rac{X_{ ext{hemiacetal}}}{X_{ ext{carbonyl}}}$
formaldehyde	0.62	2	formaldehyde	-0.09	0.3
pinonaldehyde	-5.78	2 x 10 ⁻⁸	<i>n</i> -butanal	-6.29	2 x 10 ⁻⁷
acetaldehyde	-6.46	2 x 10 ⁻⁷	acetaldehyde	-6.34	2 x 10 ⁻⁷
<i>n</i> -butanal	-6.55	9 x 10 ⁻⁹	pinonaldehyde	-6.38	2 x 10 ⁻⁷
<i>n</i> -hexanal	-7.07	2 x 10 ⁻⁹	<i>n</i> -octanal	-6.66	1 x 10 ⁻⁷
<i>n</i> -octanal	-7.09	2 x 10 ⁻⁹	<i>n</i> -hexanal	-6.69	9 x 10 ⁻⁸
<i>n</i> -decanal	-7.16	1 x 10 ⁻⁹	<i>n</i> -decanal	-6.70	9 x 10 ⁻⁸
acetone	-13.72	3 x 10 ⁻¹⁵	acetone	-13.21	$3 \ge 10^{-14}$

Table A2.1 Estimated log K values and accretion product/parent carbonyl ratio for hydrate and hemiacetal formation in liquid solution, P = 1 atm and T = 298 K.

.

^a Initial conditions: $X_{carbonyl} = 0.9$, $X_{water} = 0.1$ ^b Initial conditions: $X_{carbonyl} = 0.45$, $X_{alcohol} = 0.45$, $X_{water} = 0.1$

Acetal Formation ^a		α , β -Unsaturated Carbonyl Formation ^b			
Hemiacetal + Alcohol = Acetal		2 Carbonyl = α , β -Unsaturated Carbonyl + Water			
Parent Carbonyl	Log K	$\frac{X_{\text{acetal}}}{X_{\text{carbonyl}}}$	Parent Carbonyl	Log K	$rac{X_{ ext{unsaturated carbonyl}}}{X_{ ext{carbonyl}}}$
formaldehyde	0.62	0.1	formaldehyde	14.56	4 x 10 ⁷
<i>n</i> -butanal	-5.20	1 x 10 ⁻⁵	pinonaldehyde	5.09	2×10^2
acetaldehyde	-5.50	6 x 10 ⁻⁶	<i>n</i> -butanal	4.14	50
<i>n</i> -octanal	-5.50	6 x 10 ⁻⁶	<i>n</i> -octanal	3.37	20
<i>n</i> -hexanal	-5.54	6 x 10 ⁻⁶	<i>n</i> -hexanal	3.34	20
<i>n</i> -decanal	-5.54	6 x 10 ⁻⁶	<i>n</i> -decanal	3.27	20
pinonaldehyde	-5.77	3 x 10 ⁻⁶	acetaldehyde	2.22	10
acetone	-12.09	$2 \ge 10^{-12}$	acetone	-1.79	8 x 10 ⁻²

Table A2.2 Estimated log *K* values and accretion product/parent carbonyl ratio for acetal formation in liquid solution at equilibrium, and for α , β -unsaturated carbonyl formation in liquid solution at equilibrium; *P* = 1 atm and *T* = 298 K.

^a Initial conditions: $X_{carbonyl} = 0.45$, $X_{alcohol} = 0.45$, $X_{water} = 0.1$; $K = K_{hemiacetal} K_{acetal}$ ^b Initial conditions: $X_{carbonyl} = 0.9$, $X_{water} = 0.1$; $K = K_{\beta-hydroxycarbonyl} K_{\alpha,\beta-unsaturated carbonyl}$

.

BIOGRAPHICAL SKETCH

Kelley Barsanti was born in Albuquerque, New Mexico on July 5, 1974. Ms. Barsanti received her bachelor's degree in biology and environmental science from the University of Colorado at Boulder; she received her master's degree in environmental science and engineering from the OGI School of Science & Engineering. She has been an active member of the atmospheric aerosol research community, serving as a reviewer for Environmental Science & Technology, speaking at several national and international conferences, and publishing a number of articles in peer-reviewed journals. She also has been an active member of the OGI community, serving as president and department representative on the student council; as a speaker with OHSU Speaker's Bureau; as a judge for local, regional, and national science fairs; and as a mentor with Advocates for Women in Science, Engineering, and Mathematics. In 2005, Ms. Barsanti was awarded the Paul Clayton Student Achievement Award for her excellence in leadership, research, scholarship, and service. When not pursing academic endeavors, she spends her time pursuing culinary arts and outdoor adventures. Ms. Barsanti currently resides in Portland, Oregon with her husband, Brad Thoms.

Publications

Barsanti, K.C., Pankow, J.P., 2006. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions of atmospheric compounds—Part 3. Carboxylic and dicarboxylic acids. *Atmospheric Environment*, submitted.

Barsanti, K.C., Dabdub, D., Griffin, R.J., Seinfeld, J.H., Pankow, J.F., 2005. Comment on "Semiempirical model for organic aerosol growth by acid-catalyzed heterogeneous reactions of carbonyls". *Environmental Science & Technology* 39, 8108-8109.

Barsanti, K.C., Pankow, J.P., 2005. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions of atmospheric compounds—Part 2. Dialdehydes, methylglyoxal, and diketones. *Atmospheric Environment* 39, 6597-6607.

Barsanti, K.C., Pankow, J.P, 2004. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions of atmospheric compounds—Part 1. Aldehydes and ketones. *Atmospheric Environment* 38, 4371-4382.

Pankow, J.F., Barsanti, K.C., Peyton, D.H., 2003. Determination of the fraction of free-base nicotine in fresh smoke particulate matter from the Eclipse "cigarette" by ¹H NMR spectroscopy. *Chemical Research in Toxicology* 16, 23-27.