

A hypothesis for growth of fresh atmospheric nuclei

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[1] The formation of new atmospheric particles, roughly 1–2 nm in diameter, has drawn a lot of attention recently because of (1) their possibly negative effects on human health and (2) their potential to grow into cloud condensation nuclei, thus affecting cloud formation as well as the global radiation budget. At these small sizes, the Kelvin effect prevents condensation of any compound in sufficient abundance for producing substantial growth. But heterogeneous reactions may play a critical role in helping these nm-sized nuclei cross the huge Kelvin-effect barrier and facilitating further condensation of organic vapors. Its implications in the marine boundary layer and engine exhausts are discussed.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1050

Geochemistry: Marine geochemistry (4835, 4850); *KEYWORDS:* nucleation, condensation, Kelvin effect, marine boundary layer, exhaust, homogeneous chemical reaction

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1. Introduction

[2] The formation of new atmospheric particles has drawn a lot of attention recently because of their possibly negative effects on human health and potential to grow into cloud condensation nuclei, thus affecting cloud formation as well as the global radiation budget [Kulmala *et al.*, 2000]. Sulfuric acid-ammonia-water ternary nucleation is considered to be a likely and effective pathway for fresh particle formation in forest [Kulmala *et al.*, 2001a], marine boundary layer [Pirjola *et al.*, 2000], coastal environment [O'Dowd *et al.*, 1999], remote troposphere [Eisele and McMurry, 1997; Weber *et al.*, 1999] and vehicle exhaust [Tobias *et al.*, 2001]. However, field measurements [Weber *et al.*, 1999; Eisele and McMurry, 1997], laboratory experiments [Khalek *et al.*, 2000] and model simulations [Kerminen *et al.*, 2001; Kulmala *et al.*, 2001b] indicate that gaseous sulfuric acid concentration, while sufficient to nucleate new particles, are not sufficient for growing particles to observable sizes, or to grow nuclei quickly enough to forestall coagulation scavenging, which occurs mainly when the nuclei are still below detectable sizes (≤ 3 nm). So there must be chemical species, in addition to sulfuric acid, present to grow the nuclei into observable size and organic vapor are posited candidates [Kerminen *et al.*, 2000; Weber *et al.*, 1999, 2001; Kulmala *et al.*, 2001a; Khalek *et al.*, 2000; Tobias *et al.*, 2001].

[3] However, the Kelvin effect of these nm-sized nuclei is tremendous for organic compounds, making impossible the simple condensation of almost any organics on fresh nuclei in this early stage. Here we hypothesize that

heterogeneous reactions initiate the very early growth of nuclei.

2. Kelvin Effect on Nuclei

[4] Mirabel and Katz [1974] state that heteromolecular sulfuric acid-water nucleation leads to the formation of nuclei about 1 nm. The critical size for sulfuric acid-ammonia-water nucleation is considered to be similar or even less [Korhonen *et al.*, 1999]. The nucleation event is followed by the immediate growth of the nuclei by condensation of the nucleating species, namely sulfuric acid, water and/or ammonia. Considering that it takes seven times more materials to grow the same number of nuclei from 1 nm to 2 nm than to nucleate, the growth cannot be much more than this, as indicated by nucleation events in remote continental sites [Eisele and McMurry, 1997], that is, the nucleating species are unlikely to grow nuclei to currently detectable sizes (≤ 3 nm). Despite of the lack of sufficient observational support, we speculate that this phenomenon also applies in urban plumes because (1) although the sulfuric acid concentrations are much higher than those in the clean environments, the preexisting particle concentrations are also higher, providing much higher condensational sinks for sulfuric acids; (2) higher sulfuric concentrations lead to higher nucleation rates that produce more fresh nuclei, which share the condensation of sulfuric acid to yield a small single-particle growth.

[5] As mentioned previously, the observed rapid growth rates of nuclei are likely the result of condensation of organic vapors. Their condensation rate depends on the difference between the compound partial pressures, P_i , and the Kelvin-adjusted vapor pressures, $P^0 \cdot Ke$, where P^0 is the bulk phase vapor pressure of the condensing species and Ke the Kelvin factor for the species. Because of the Kelvin effect, equilibrium vapor pressures increase with decreasing

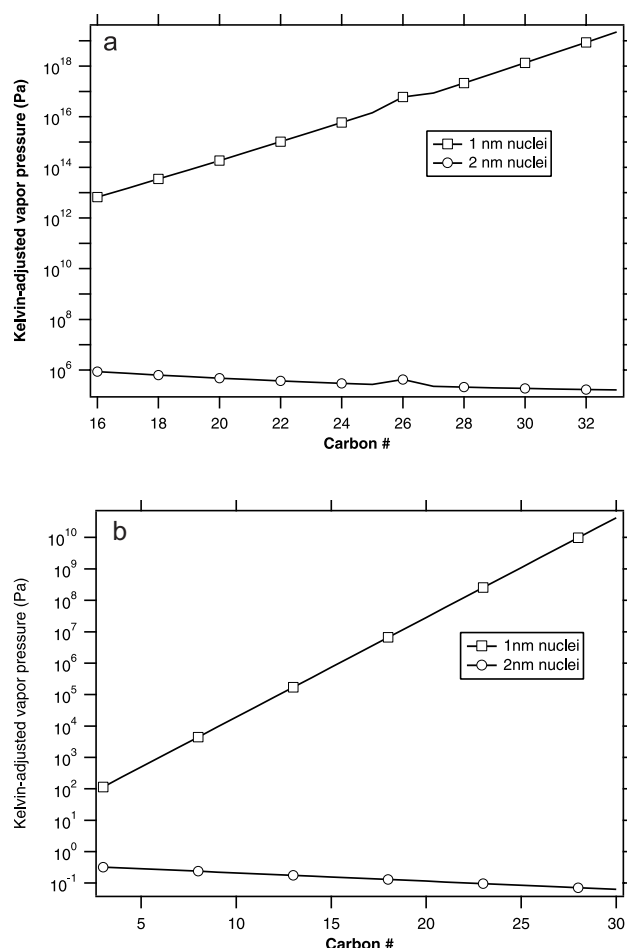


Figure 1. The Kelvin-adjusted vapor pressures of (a) alkanes and (b) diacids as functions of carbon number for 1 and 2 nm nuclei.

particle size and increasing molar volume of the condensing compound. (Note that molar volume refers to the volume occupied by one mole of the compound in condensed phase.) Therefore, it is expected that the nuclei initially grow by condensation of nonvolatile or low volatile compounds, with condensation of more volatile components increasing as the particle size increases.

[6] How large is the Kelvin effect on the 1 ~ 2 nm nuclei? The Kelvin factor, Ke , is given by

$$Ke = \exp(4\sigma M/RT\rho D_p),$$

where σ is the surface tension of the nuclei, M and ρ are the molar mass and density of the condensing species, respectively, R the gas constant, T the temperature, D_p the nuclei size. Although surface tension will decrease as more soluble organics condense, for the very early growth of the nuclei, σ is dominated by the value for the nucleating species, at least 70 dyn cm^{-1} , given that the dominance of sulfuric acid and ammonium sulfate water solution are both higher than this value [Pruppacher and Klett, 1997]. M and ρ give the molar volume of the condensing species, making Ke vary from species to species, but with the general trend that Ke increases with molar mass.

[7] As we have noted, what governs condensation is the comparison of partial pressures to the Kelvin-adjusted vapor pressures, while the latter has two components, P^0 and Ke . For organics, generally P^0 decreases as molar mass increases, an opposite trend to that of Ke . Let us now evaluate the Kelvin-adjusted vapor pressures of two condensable organic classes, the n-alkanes and diacids.

[8] N-alkanes are common organic compounds in both fuel and oil, and high carbon number alkanes are posited contributors to nuclei growth in engine exhausts [Tobias *et al.*, 2001]. Figure 1a shows the Kelvin-adjusted vapor pressures, $P^0 \cdot Ke$, extrapolated to 293 K from the empirical formula introduced by Lemmon and Goodwin [2000], which are in good agreement with the data provided by Liang and Pankow [1996], as functions of carbon numbers. Dicarboxylic acids, ubiquitous compounds in the ambient atmosphere and engine exhausts [Kawamura *et al.*, 1996], are known to have much lower vapor pressures than n-alkanes for the same carbon number. We calculated the vapor pressure based on Makar [2001] and plotted the equivalent gas-phase concentrations as functions of carbon number shown as Figure 1b. Although the bulk-phase vapor pressures, P^0 , decrease with carbon atom number, the huge values presented in Figure 1 are a result of dramatic increases of the Kelvin factors with molar volume for such small particles. We see that the Kelvin barrier is so huge that neither higher carbon number alkanes nor diacids can condense on 1–2 nm nuclei.

[9] For small ensembles such as nuclei, there are always random fluctuations for any physical property, as with the Kelvin factor, and it has been posited that these fluctuations may overcome the barrier. However, it is unlikely fluctuations can explain nuclei growth when there are so many orders of magnitude differences between ambient concentration and equilibrium vapor pressure values needed for growth.

3. Atmospheric Nuclei Growth Hypothesis

[10] The dominant influence of the Kelvin effect for these small particles implies that nuclei growth favors the condensation of compounds with both low volatility and low molar volume. If water soluble or acid soluble organic compounds condense, they lower the nuclei surface tension, which facilitates condensation of higher volatility compound. It is hard to find such organic compounds, given the fact that the vapor pressures, as well as solubility, of most organic compounds decrease as their molar volume increases. Yet, to the best of our knowledge, organics are the only compounds in sufficient concentration in exhaust plumes or the clean environment that can lead to the observed growth. So there must be some mechanisms, other than simple condensation, helping nuclei grow. Such mechanisms only need to grow the nuclei a small amount to make the Kelvin effect drop sharply because of its exponential relationship with nuclei size. Then other organic may condense. The timescale for the mechanism must be very short, usually within an hour, to prevent nuclei from coagulating with preexisting larger particles [Kerminen *et al.*, 2001]. The mechanisms to be proposed here need only act on the nuclei for a very short time, since they are just necessary for their roles in crossing the Kelvin effect barrier.

Table 1. Thermodynamic State of Nuclei in the Engine Exhausts Estimated by AIM Model

Experiment	Gasoline Engines		Diesel Engines			
	G1	G2	D1	D2	D3	D4
INPUT (moles/m ³)						
Water activity	0.1	0.2	0.1	0.2	0.1	0.1
Hydrogen	2.000000E-12	4.00000E-12	7.00000E-09	1.50000E-08	7.00000E-08	1.00000E-10
Ammonium	1.999998E-06	1.999996E-06	1.99300E-06	1.98500E-06	1.93000E-06	1.99000E-08
Sulfate	1.000000E-06	1.000000E-06	1.00000E-06	1.00000E-06	1.00000E-06	1.00000E-08
Liquid phase Concentration (moles/m ³)						
H(aq)	1.49260E-12	1.89340E-12	4.96140E-09	6.11740E-09	2.24630E-08	6.91730E-11
pH	3.55	3.99	0.04	0.49	-0.54	-0.11
NH4(aq)	2.00000E-06	2.00000E-06	1.99300E-06	1.98500E-06	1.93000E-06	1.99000E-08
HSO4(aq)	5.07390E-13	2.10660E-12	2.03860E-09	8.88260E-09	4.75370E-08	3.08270E-11
SO4(aq)	1.00000E-06	1.00000E-06	9.97960E-07	9.91120E-07	9.52460E-07	9.96920E-09
H2O(l)	2.95700E-07	1.03830E-06	2.99280E-07	1.05480E-06	3.62790E-07	3.01090E-09
Gas phase concentration (moles/m ³)						
NH3(g)	1.61800E-03	1.49300E-03	4.24500E-07	4.03700E-07	5.61900E-08	2.88500E-07
H2SO4(g)	2.36500E-27	1.83400E-27	3.41200E-20	2.47100E-16	1.86600E-18	7.36200E-20

Heterogeneous chemical reactions between organic vapors and nuclei are likely candidates.

3.1. Thermodynamic State of the Nuclei

[11] First let us explore the chemical characteristic of sulfuric acid-water-ammonium nuclei in marine boundary layer. Several models and observations show that the marine boundary layer accumulation mode particles are very acidic [Fridlind and Jacobson, 2000], and Bates *et al.* [2001] found that submicron ammonium sulfate aerosol was acidic over Atlantic. Those findings may suggest that the nuclei are also acidic. The Kelvin effect serves to force volatile compounds, such as water and ammonia to evaporate from particles, such that a small ammonium deficit may produce a low pH.

[12] Next we investigated engine exhausts. The AIM model, which calculates the phase equilibrium of inorganic aerosol systems relevant to the atmosphere [Clegg *et al.*, 1998] (see <http://mae.ucdavis.edu/wexler/aim>), was used. Two major assumptions have been made in our application: (1) the equilibrium between ammonia and ammonium is quickly achieved and (2) there is no solid phase in the nuclei. The first assumption is reasonable because both nuclei and preexisting particles provide large surface areas for condensation. The second one is made based on the fact the formation of solid salt phases requires a high supersaturation ratio [Martin, 2000], which certainly exists in nuclei, but the solid phase must also nucleate and this is unlikely in such a small volume. Since AIM does not consider the Kelvin effect explicitly, we supply inputs of an equivalent bulk phase. The Kelvin factors of water and ammonia have similar magnitude, which are around 10 for a 1 nm nucleus. So the equivalent relative humidity is around one tenth of that in the ambient environment or exhaust, as is the equivalent gas-phase ammonium concentration.

[13] Using a fuel sulfur mass content of 40 ppm, assumed sulfur to sulfuric acid conversion rate of 4%, tailpipe temperature of 500 K and dilution ratio of 1:10, we can estimate the sulfuric acid concentration in the exhaust to be 10^{-6} moles m^{-3} . Since sulfuric acid has sufficient low vapor pressure, we can assume that almost all the sulfuric acid is in the particle phase after it cools to ambient conditions. Ammonia concentrations vary tremendously depending on engine type. Gasoline engines have very high NH_3 emissions because

Three-Way Catalyst (TWC) systems are a major source of ammonia, with concentrations around 40 ppm [Baum *et al.*, 2001]. Diesels do not use TWC systems so the NH_3 emission is significantly lower, with an upper limit we estimate to be 10 ppb [Williams *et al.*, 2000].

[14] Table 1 shows particle equilibrium composition calculated with AIM. A 10% water activity was chosen as a worst case—one tenth of 100% RH—a lower RH would predict even lower pH values. All cases predict nearly neutralized nuclei, that is, the hydrogen ion concentration is rather small compared with ammonium and sulfate concentration. But since the water concentration is also small, low pH values are predicted in all cases. In diesel engine exhaust, pH values are equal or below zero, while in the gasoline power engine results (G1 and G2), the particle phase pH value is around 3. Cases where gas phase NH_3 is one order of magnitude lower (D3) and where H_2SO_4 is two orders of magnitude lower (D4) were also tested, which may correspond to much lower sulfur content or higher dilution ratio, but the pH values do not change very much and are still very low, as long as the water activity is low, indicating a buffering by the sulfate-bisulfate equilibrium. Note that a higher water activity (D2) leads to higher pH value.

[15] By using AIM model for small nuclei, we are making a continuum approximation where it may not necessarily apply, so the results should be considered to be ensemble statistical averaged values. For example, there are only tens, or maybe hundreds, of molecules in a nucleus, so that most nuclei will have a neutral pH at a given time, but a fraction of the nuclei will have a hydrogen ion excess and a resulting pH sufficiently low to promote the reactions, to be discussed in the next section. This is not the case for nuclei in the gasoline exhausts, since the ratio of proton to sulfates or ammonium is so small there is little chance for free protons. We will discuss this situation later. In summary, the nuclei in diesel exhaust and the marine boundary layer often have high-activity protons, while nuclei in gasoline engine exhaust are highly neutralized.

3.2. Heterogeneous Reactions of Organics With Nuclei

[16] It has been well-known for decades that some organic compounds are soluble in acid solution, and that these acids also catalyze a range of organic reactions [Neckers and

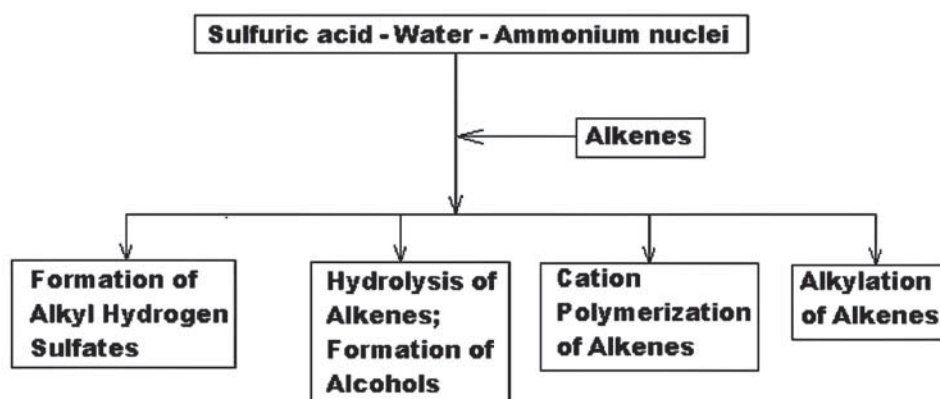


Figure 2. The possible reaction mechanism between alkenes and sulfuric acid.

Doyle, 1977]. A recent experimental study conducted by Jang and Kamens [2001] showed aerosol growth by heterogeneous aldehyde reactions via a hydration, polymerization process, and hemiacetal/acetal formation from the reaction of aldehydes with alcohols. These aldehyde heterogeneous reactions were accelerated in the presence of an acid catalyst, H_2SO_4 , and lead to higher aerosol yields than when H_2SO_4 was not present in the seed aerosol. They concluded that aldehydes, which are produced by atmospheric photochemical reactions, can significantly contribute to secondary aerosol formation through heterogeneous reactions in the presence of a particle-phase acid catalyst. Experiments were also conducted with α -pinene and isoprene, similar SOA enhancements were observed (R. M. Kamens, personal communication, 2001).

[17] We believe that similar reactions could also happen in H_2SO_4 concentrated nuclei, contributing to their growth. Next we explored further the possibility of the reactions between alkenes and sulfuric acid, illustrated as Figure 2, and their implications for the growth of nuclei.

3.2.1. Addition Reactions of Alkenes

[18] The carbon-carbon double bond of an alkene is an unsaturated group and will undergo addition reactions [Neckers and Doyle, 1977]. There are two pathways for the reaction of alkenes and sulfuric acid—addition of water and addition of acid—and they are in a dynamic equilibrium: alkyl hydrogen sulfates are easily hydrolyzed by water to produce alcohols; alcohol can be dehydrated back to alkyl hydrogen sulfates. Generally, concentrated sulfuric acid and high temperature favor the addition of acid, whereas the dilute sulfuric acid and low temperature favor the addition of water [Morrison and Boyd, 1975]. Since the nuclei are highly concentrated sulfuric acid, addition of acid is the likely reaction.

[19] Alkyl hydrogen sulfates have several properties that make them good candidates for promoting nuclei

growth. Once they come in contact, alkene molecules tend to react with sulfuric acid to form alkyl hydrogen sulfate on the nuclei surface. Since alkyl hydrogen sulfate and sulfuric acid are similar in volatility and solubility [Noller, 1957; Neckers and Doyle, 1977], they remain in the particle phase. Then nuclei grow and surface tension decreases as a result of surfactant effect of alkyl sulfates, both of which decrease the Kelvin effect. The uptake of alkenes and alkylenes by acid has been briefly proposed by Yu *et al.* [1999] as a possible growth mechanism in high sulfur content jet fuel exhaust. We have shown in the previous section that the nuclei are very acidic even when low sulfur content fuels are used. So alkyl hydrogen sulfate is the likely product regardless of fuel sulfur content, as long as the pH is sufficiently low. Another possible pathway is that condensation or nucleation of alkyl sulfates formed by gas-phase reactions of alkenes and sulfuric acid, given the low volatility and low surface tension of alkyl hydrogen sulfates.

3.2.2. Cation Polymerization and Alkylation of Alkenes

[20] Cation polymerization is usually initiated by acids and the initiator is the hydrogen cation. A pair of electrons, from the carbon-carbon double bond will be attracted to this cation, and will leave the carbon-carbon double bond to form a single bond with the initiator. This leaves one of the former double bonded carbons at a loss for electrons, and carrying a positive charge. This new cation will react with a second monomer molecule in the same manner as the initiator reacted with the first monomer molecule. The growing carbonium ion may either eject a proton to form an alkene or combine with an anion to terminate the process. Alkylation has the same initiation step as the polymerization, but the fate of the carbonium ion is different in the propagation step. The alkane is involved as a hydride donor, transferring a hydrogen with its pair of electrons to the cation. Then a

Table 2. Concentrations of Ethylene and Propylene in Engine Exhausts and Urban Atmosphere^a

Alkenes	Ground Level Concentrations			In the Exhaust (% of Emitted HCs)			Atmosphere Half-Lives (days)		
	Urban Air	Downtown LA	East San Gabriel Valley	Reciprocating Engine	Rotary Gasoline Engine	Diesel Engine	Reactions With OH	Reactions With O ₃	Reactions With HO ₂
Ethylene	12 ~ 250 ppb	20 ~ 102 ppb	15 ~ 37 ppb	14.1	8.1	14.5	1	4.2	<13,000
Propylene	5–50 µg/l	13 ~ 64 ppb	10 ~ 24 ppb	7.3	5.3	6.3	0.3	0.6	<13,000

^aFrom Verschueren [1996].

Table 3. Average Concentrations of Alkenes in Marine Boundary Layer at Cape Grim (GC) and Mace Head (MH)^a

	Ethene		Propene		Isoprene	
	CG	MH	CG	MH	CG	MH
Mean daytime value (ppt)	9.3	21	5.2	25.1	5.7	8.4
Mean nighttime value (ppt)	4.8	11.1	2.1	4.6	<1.6	<2.0

^aFrom Lewis *et al.* [2001].

new alkane is formed and a new cation is regenerated [Neckers and Doyle, 1977]. Whether alkenes react via polymerization or alkylation depends on the relative ease with which electrons are obtained from a double or single bond—certainly preferring the double.

[21] Note that we have investigated the possibility of formation of alkyl hydrogen sulfates, which are also acidic and can promote polymerization, too. Although there is insufficient evidence to estimate the rate of polymerization, clearly, long polymers have very low vapor pressures so will remain in nuclei if they form.

3.3. Existence of Alkenes in the Atmosphere

[22] A necessary ingredient for growth via the proposed mechanism is gas phase alkenes at sufficient concentrations. Tables 2 and 3 showed typical concentrations for the environment that we are considering.

4. Discussion and Conclusion

[23] The processes we have described depend on three timescales: τ_{heter} , the timescale for the acid-organic heterogeneous reactions; τ_{coag} , the coagulation timescale for fresh nuclei; and τ_{alkenes} , the lifetime of alkenes due to their major sinks in the atmospheric—reactions with hydroxyl radicals and ozone [Seinfeld and Pandis, 1998]. Although the detailed investigation of τ_{heter} is beyond the scope of the current study, a qualitatively analysis can give us some insight into these competing processes. The successful growth process requires that τ_{heter} is shorter than both τ_{coag} and τ_{sink} , otherwise either alkenes or fresh nuclei will diminish before the proposed heterogeneous reactions can contribute to the nuclei growth. Thus, τ_{coag} and τ_{sink} set the upper limit for τ_{heter} . Next we discuss it under different circumstances.

4.1. Clean Environment

[24] Our study suggests that the growth of nuclei is limited by both acid-organic heterogeneous reactions and the availability of nonvolatile organics. Thus a successful production of CCN from nucleation may take the following steps: (1) formation of nuclei and their immediate growth by water, sulfuric acid and ammonia condensation, (2) heterogeneous reactions to grow these nuclei from around 1~2 nm to the size where condensation of organics is possible, and (3) condensation of organics, starting with those of lowest volatility and proceeding to those of higher volatility, to grow particles to CCN size. In the marine boundary layer, the hydroxyl radical concentration is on the order of 10^6 molecules cm^{-3} and ozone around 10^{12} molecules cm^{-3} [Heikes *et al.*, 1996; Davis *et al.*, 2001]. Using the rate constants listed by Atkinson [1994], we found τ_{alkenes} is about 10^4 – 10^6 s, while τ_{coag} was shown to be 10^2 to 10^4 s [Kerminen *et al.*, 2001]. Thus, the growth rate due to the

heterogeneous reaction must proceed faster than about 10^2 to 10^4 seconds to be effective before coagulation removes the nuclei.

4.2. Diesel Exhausts

[25] In the diesel exhausts, due to the presence of plenty of organic, the growth of nuclei is mainly limited by heterogeneous reactions and coagulation losses of nuclei. τ_{coag} varies over a large range due to dilution conditions and accumulation mode particles emission rates. We have shown that the acidity of nuclei does not change much with fuel sulfur contents, which may help to explain the observed insensitivity of measured particle number concentrations to fuel sulfur contents [Khalek *et al.*, 2000].

4.3. Gasoline Engine Exhausts

[26] As far as we know, only the work of Graskow *et al.* [2000] suggests nucleation in gasoline exhaust, but from our analysis, the proposed heterogeneous organic reactions can hardly proceed in the nuclei because high ammonia concentrations from TWC systems neutralize nucleus acidity. Ammonia will not contribute significantly to the nuclei growth since its condensation is limited when the nuclei is neutralized. So what mechanism helps the nuclei cross the Kelvin effect barrier? One possibility is that alkyl hydrogen sulfates, produced by gas-phase reactions between alkenes and sulfuric acid, condense on the nuclei to lower the surface tension. But one question remains: most alkyl sulfates will transform to ammonium alkyl sulfate as a result of high ammonia concentrations. The surface tension of ammonium alkyl sulfate is a complicated function of its concentration and could be as high as that of ammonium sulfate. In that circumstance surface tension of the nuclei will not be reduced and the growth of nuclei in the gasoline engine exhausts can only due to the additional volume contributed by the alkyl group.

[27] We have demonstrated the viability of some possible mechanisms for atmospheric nuclei growth due to organic reactions catalyzed by sulfuric acid. Our mechanism is certainly not the only one since there is nucleation and growth in situations without sulfuric acid or where sulfuric acid is neutralized by ammonia. But in many atmospheric situations, as indicated by numerous studies, there is nucleation of sulfuric acid and subsequent rapid growth that cannot be explained by the nucleating species so there must be substantial quantities of a condensable compound. Nevertheless, the large magnitude of the Kelvin effect prevents the simple condensation of even very large organic compounds emitted into exhausts. Then heterogeneous reactions may play a critical role in helping these nm-sized nuclei cross the huge Kelvin-effect barrier and facilitating further condensation of organic vapors.

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References

- Atkinson, R., Gas-phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data Monogr.*, 2, 1–216, 1994.
 Bates, T. S., P. K. Quinn, D. J. Coffman, J. E. Johnson, T. L. Miller, D. S. Covert, A. Wiedensohler, S. Leinert, A. Nowak, and C. Neususs, Regional physical and chemical properties of the marine boundary layer aerosol

- across the Atlantic during Aerosols99: An overview, *J. Geophys. Res.*, 106(D18), 20,767–20,782, 2001.
- Baum, M. M., E. S. Kiyomiya, S. Kumar, A. M. Lappas, V. A. Kapinus, and H. C. Lord, Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy, 2, Direct on-road ammonia measurements, *Environ. Sci. Technol.*, 35(18), 3735–3741, 2001.
- Clegg, S. L., P. Brimblecombe, and A. S. Wexler, A thermodynamic model of the system H-NH₄-Na-SO₄-NO₃-Cl-H₂O at 298.15 K, *J. Phys. Chem. A*, 102, 2155–2171, 1998.
- Davis, D., et al., Marine latitude/altitude OH distributions: Comparison of Pacific Ocean observations with models, *J. Geophys. Res.*, 106(D23), 32,691–32,707, 2001.
- Eisele, F. L., and P. H. McMurry, Recent progress in understanding particle nucleation and growth, *Philos. Trans. R. Soc. London, Ser. B*, 352(1350), 191–200, 1997.
- Fridlind, A. M., and M. Z. Jacobson, A study of gas-aerosol equilibrium and aerosol pH in the remote marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, 105(D13), 17,325–17,340, 2000.
- Graskow, B. R., D. B. Kittelson, M. R. Ahmadi, and J. E. Morris, Influence of fuel additives and dilution conditions on the formation and emission of exhaust particulate matter from a direct injection spark ignition engine, *SAE Tech. Pap.*, 2000-01-2018, 2000.
- Heikes, B., M. H. Lee, D. Jacob, R. Talbot, J. Bradshaw, H. Singh, D. Blake, B. Anderson, H. Fuelberg, and A. M. Thompson, Ozone, hydroperoxides, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic, *J. Geophys. Res.*, 101(D19), 24,221–24,234, 1996.
- Jang, M., and R. M. Kamens, Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci. Technol.*, 35(24), 4758–4766, 2001.
- Kawamura, K., S. Steinberg, and I. R. Kaplan, Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern California wet precipitations: Comparison of urban and nonurban samples and compositional changes during scavenging, *Atmos. Environ.*, 30(7), 1035–1052, 1996.
- Kerminen, V.-M., A. Virkkula, R. Hillamo, A. S. Wexler, and M. Kulmala, Secondary organics and atmospheric cloud condensation nuclei production, *J. Geophys. Res.*, 105(D7), 9255–9264, 2000.
- Kerminen, V. M., L. Pirjola, and M. Kulmala, How significantly does coagulation scavenging limit atmospheric particle production?, *J. Geophys. Res.*, 106(D20), 24,119–24,125, 2001.
- Khalek, I. A., D. B. Kittelson, and F. Brear, Nanoparticle growth during dilution and cooling of diesel exhaust: Experimental investigation and theoretical assessment, *SAE Tech. Pap.*, 2000-01-0515, 2000.
- Korhonen, P., M. Kulmala, A. Laaksonen, Y. Viisanen, R. McGraw, and J. H. Seinfeld, Ternary nucleation of H₂SO₄, NH₃, and H₂O in the atmosphere, *J. Geophys. Res.*, 104(D21), 26,349–26,353, 1999.
- Kulmala, M., L. Pirjola, and J. M. Makela, Stable sulphate clusters as a source of new atmospheric particles, *Nature*, 404(6773), 66–69, 2000.
- Kulmala, M., et al., Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR), *Tellus, Ser. B*, 53, 324–343, 2001a.
- Kulmala, M., M. Dal Maso, J. M. Makela, L. Pirjola, M. Vakeva, P. Aalto, P. Miiikkulainen, K. Hameri, and C. D. O'Dowd, On the formation, growth and composition of nucleation mode particles, *Tellus, Ser. B*, 53(4), 479–490, 2001b.
- Lemmon, E. W., and A. R. H. Goodwin, Critical properties and vapor pressure equation for alkanes C_nH_{2n+2}: Normal alkanes with n ≤ 36 and isomers for n = 4 through n = 9, *J. Phys. Chem. Ref. Data*, 29(1), 1–39, 2000.
- Lewis, A. C., L. J. Carpenter, and M. J. Pilling, Nonmethane hydrocarbons in Southern Ocean boundary layer air, *J. Geophys. Res.*, 106(D5), 4987–4994, 2001.
- Liang, C. K., and J. F. Pankow, Gas/particle partitioning of organic compounds to environmental tobacco smoke: Partition coefficient measurements by desorption and comparison to urban particulate material, *Environ. Sci. Technol.*, 30(9), 2800–2805, 1996.
- Makar, P. A., The estimation of organic gas vapour pressure, *Atmos. Environ.*, 35(5), 961–974, 2001.
- Martin, S. T., Phase transitions of aqueous atmospheric particles, *Chem. Rev.*, 100(9), 3403–3453, 2000.
- Mirabel, P., and J. L. Katz, Binary homogeneous nucleation as a mechanism for the formation of aerosols, *J. Chem. Phys.*, 60(3), 1138–1144, 1974.
- Morrison, R. T., and R. N. Boyd, *Organic Chemistry*, 3rd ed., Allyn and Bacon, Needham Heights, Mass., 1975.
- Neckers, D. C., and M. P. Doyle, *Organic Chemistry*, John Wiley, New York, 1977.
- Noller, C. R., *Chemistry of Organic Compounds*, 2nd ed., W. B. Saunders, Philadelphia, Pa., 1957.
- O'Dowd, C. D., J. A. Lowe, and M. H. Smith, Coupling sea-salt and sulphate interactions and its impact on cloud droplet concentration predictions, *Geophys. Res. Lett.*, 26(9), 1311–1314, 1999.
- Pirjola, L., C. D. O'Dowd, I. M. Brooks, and M. Kulmala, Can new particle formation occur in the clean marine boundary layer?, *J. Geophys. Res.*, 105(D21), 26,531–26,546, 2000.
- Pruppacher, H. R., and J. D. Klett, *Microphysics of Clouds and Precipitation*, Kluwer Acad., Norwell, Mass., 1997.
- Seinfeld, J. H., and S. N. Pandis, *Atmospheric Chemistry and Physics*, John Wiley, New York, 1998.
- Shi, J. P., and R. M. Harrison, Investigation of ultrafine particle formation during diesel exhaust dilution, *Environ. Sci. Technol.*, 33(21), 3730–3736, 1999.
- Streitwieser Jr., A., and C. H. Heathcock, *Introduction to Organic Chemistry*, 2nd ed., MacMillan, Old Tappan, N. J., 1981.
- Tobias, H. J., D. E. Beving, P. J. Ziemann, H. Sakurai, M. Zuk, P. H. McMurry, D. Zarling, R. Waytulonis, and D. B. Kittelson, Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal desorption particle beam mass spectrometer, *Environ. Sci. Technol.*, 35(11), 2233–2243, 2001.
- Verschueren, K., *Handbook of Environmental Data on Organic Chemicals*, 3rd ed., Van Nostrand Reinhold, New York, 1996.
- VonNiederhausen, D. M., G. M. Wilson, and N. F. Giles, Critical point and vapor pressure measurements at high temperatures by means of a new apparatus with ultralow residence times, *J. Chem. Eng. Data*, 45(2), 157–160, 2000.
- Weber, R. J., P. H. McMurry, R. L. Mauldin, D. J. Tanner, F. L. Eisele, A. D. Clarke, and V. N. Kapustin, New particle formation in the remote troposphere: A comparison of observations at various sites, *Geophys. Res. Lett.*, 26(3), 307–310, 1999.
- Weber, R. J., G. Chen, D. D. Davis, R. L. Mauldin, D. J. Tanner, F. L. Eisele, A. D. Clarke, D. C. Thornton, and A. R. Bandy, Measurements of enhanced H₂SO₄ and 3–4 nm particles near a frontal cloud during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, 106(D20), 24,107–24,117, 2001.
- Williams, P. I., et al., Aerosol development and interaction in an urban plume, *Aerosol Sci. Technol.*, 32(2), 120–126, 2000.
- Yu, F. Q., R. P. Turco, and B. Karcher, The possible role of organics in the formation and evolution of ultrafine aircraft particles, *J. Geophys. Res.*, 104(D4), 4079–4087, 1999.

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