

Comment on "Semiempirical Model for Organic Aerosol Growth by Acid-Catalyzed Heterogeneous Reactions of Carbonyls"

Jang et al. (1) report measurements of organic particulate matter (OPM) formed in the presence of acidic seed aerosols using both a flow reactor and a Teflon chamber and examine their data using two modeling approaches. The study is a continuation of work by Jang et al. (2) on whether acidity in atmospheric PM can promote the formation of OPM by "heterogeneous" reaction of a variety of relatively volatile (C_5 – C_{10}) aldehydes and ketones. Jang et al. (1) state that (a) "no predictivity power was achieved" for their experimental systems when using the absorptive partitioning model of Pankow (3) and (b) "These results suggest that semiempirical approaches can vastly improve our ability to predict the organic aerosol growth of a variety of different carbonyls in the presence of inorganic acid. For equilibrium conditions in the atmosphere this approach can be applied directly." In our view, (a) Jang et al. (1) misapplied the Pankow (3) model and (b) their proposed "semiempirical model" is inherently a characterization of the kinetics of OPM formation (see their eqs 5–12) under specific conditions and so is not easily applicable to the prediction of how much OPM will form under other kinetic conditions and certainly not at equilibrium in the atmosphere.

Organic aerosol formation yield Y is typically defined as (e.g., see ref 4)

$$Y = M/\Delta C \quad (1)$$

where the units for both M and ΔC are mg/m^3 (or $\mu\text{g}/\text{m}^3$) and M is a measure of the secondary PM formed upon reaction of ΔC worth of gas-phase parent compound (for a hydrocarbon, ΔHC). In contrast, Jang et al. (1) define their "first-order relative aerosol yield" Y_1 as

$$Y_1 = (M_{\text{mix}} - M_{\text{seed}})/(10^3 K_{p,i} C_i M_{\text{seed}}) \quad (2)$$

where the factor 10^3 is included here so that the gas/particle (G/P) partitioning constant $K_{p,i}$ has its common units of $\text{m}^3/\mu\text{g}$ rather than m^3/mg as utilized by Jang et al. (1). (PM in the atmosphere is typically present at $\mu\text{g}/\text{m}^3$ levels, not mg/m^3 levels.) M_{mix} (mg/m^3) is the level of total PM, M_{seed} (mg/m^3) is the level of seed aerosol, and C_i (mg/m^3) is the initial concentration of reacting parent carbonyl compound i . The quantity $10^3 K_{p,i} C_i M_{\text{seed}}$ (mg/m^3) is intended by Jang et al. (1) to give a prediction, based on the model of Pankow (3), of the amount of organic mass found in the PM phase by G/P partitioning of the parent compound i to the initial seed aerosol.

Y_1 is a flawed and misleading definition of OPM yield. First, it is not reaction-based (C is involved rather than ΔC), and therefore it is inconsistent with the extensive literature on OPM yields in reacting aerosol systems. Second and more problematically, the Pankow (3) model is assigned the task of predicting the formation of total OPM when only the highly volatile parent carbonyl is presumed to partition to the seed aerosol. Indeed, (a) even when their C_i values reach $20,000 \text{ mg}/\text{m}^3$ ($\sim 5000 \text{ ppm}$), the high vapor pressures of the parent compounds will not permit formation of any significant amount of OPM by partitioning to the seed particles, and (b) at such high concentrations, the probability increases that

at least some kind of OPM-forming reaction will occur (whether acid-catalyzed or not). Therefore, the poor prediction of OPM formation by Y_1 is neither surprising nor is it due to a breakdown of the Pankow (3) model. Proper application of the Pankow (3) model requires a multicomponent consideration of *all* compounds in the system as initially described by Pankow (5) and subsequently applied by others.

Jang et al. (1) may choose to defend their Y_1 parameter by stating that its solitary purpose is to demonstrate that the studied carbonyl compounds can only produce OPM by reaction, i.e., not just by partitioning of the parent compound at C_i . In that case, we still note that their calculations of $10^3 K_{p,i} C_i M_{\text{seed}}$ assume that each parent compound partitioned to a dilute aqueous seed solution (i.e., according to $K_{p,i}$ values calculated for partitioning to water) rather than to the nondilute seed solutions that would in fact have been achieved at the relative humidities used.

In the development of their "semiempirical model", Jang et al. (1) assume that (a) their flow reactor experiments reflected steady-state production of the "aerosol mass increase" $\text{OM} = M_{\text{mix}} - M_{\text{seed}}$ (note that, neglecting water, $\text{OM} = \text{OPM}$) and (b) OM production occurred by polymerization in the PM phase at a rate proportional to C_s^2 where C_s is the PM-phase concentration of reactant i . Regarding the first assumption, the group $\text{OM}/(M_{\text{seed}} 10^3 \text{MW}_i)$ is used as a seed-normalized version of the steady-state "aerosol mass increase". Regarding the second assumption, C_s is expressed as $10^3 K_{p,i} C_i / (10^3 \text{MW}_i)$. (The factor of 10^3 in the numerator has been added here for the same reason it was added in eq 2. Each factor of 10^3 appearing with a MW_i is used (but not expressed) by Jang et al. (1) to obtain units of mg/mol .) Jang et al. (1) then argue that normalizing $\text{OM}/(M_{\text{seed}} 10^3 \text{MW}_i)$ by C_s^2 will give a second "yield" parameter Y_2 and that Y_2 should be proportional to their hypothesized apparent second-order rate constant k_{app}' for their hypothesized polymerization process

$$Y_2 = \frac{\text{OM}/(M_{\text{seed}} 10^3 \text{MW}_i)}{C_s^2} = \frac{\text{OM}/(M_{\text{seed}} 10^3 \text{MW}_i)}{(10^3 K_{p,i} C_i / 10^3 \text{MW}_i)^2} = \frac{10^3 \text{MW}_i (\text{OM})}{M_{\text{seed}} (10^3 K_{p,i} C_i)^2} \propto k_{\text{app}}' \quad (3)$$

Jang et al. (1) calculate experimental Y_2 values from their data by eq 3 and fit those values using various linear regressions involving a total of five different variables. The fitting variables include K_{hyd} , and $K_{\text{BH}+}$, which are, respectively, the equilibrium constant for hydration of i and the acidity constant for protonated i . That Jang et al. (1) should succeed in fitting Y_2 using this many different variables is not surprising. Indeed, we note that (a) at the C_i used by Jang et al. (1) calculations carried out according to Barsanti and Pankow (6) would predict formation of significant OPM by aldol condensation products for at least some of the compounds considered and (b) log–log linear free energy relationships (LFERs) can be found between equilibrium constants for the bimolecular formation of two different aldol condensation products (the hydroxyl carbonyl (hc) and the unsaturated carbonyl (uc)) and parameters such as K_{hyd} and $K_{\text{BH}+}$. Regarding LFERs, we have used the method of Benson (7) as implemented using the CHETAH 2002 algorithm (8) to estimate the values of the standard free energy of formation ΔG_f° needed to calculate the reaction ΔG° values underlying

two liquid-phase equilibrium constants: $K_{hc} = x_{hc}/x_i^2$ and $K_{uc} = x_{uc}x_{H_2O}/x_i^2$. (Each x is a mole fraction.) For the compounds 2,4-hexadienal, octanal, 2-hexenal, hexanal, 2-octanone, 2,4-pentanedione, and mesityl oxide, the paired values for $\log K_{hc}$ and $\log K_{hyd}$ were here found to be: 1.25, 1.00; 3.07, 0.40; 1.10, 1.00; 3.27, 0.40; -1.50, 2.90; 0.06, 2.90; -2.11, 2.90 ($r^2 = 0.86$). Similarly, paired values for $\log K_{uc}$ and $\log K_{BH+}$ were found to be: -5.42, 2.20; 6.48, 6.00; -5.38, 3.80; 6.48, 6.00; 1.06, 5.20; -0.69, 2.90; -9.16, 2.90 ($r^2 = 0.75$). (The values for $\log K_{hyd}$ and $\log K_{BH+}$ are taken from Janget al. (1).) That values of Y_2 should correlate with parameters of the type considered by Jang et al. (1) *will not*, however, make Y_2 useful as a tool that can be applied in the prediction of OPM formation under concentration, residence time, steady-state, non-steady-state, and temperature conditions that are different from those used to achieve the results reported for their experiments.

Acknowledgment. This work was funded in part by the Electric Power Research Institute.

Literature Cited

- (1) Jang, M.; Czoschke, N. M.; Northcross, A. L. Semiempirical model for organic aerosol growth by acid-catalyzed heterogeneous reactions of organic carbonyls. *Environ. Sci. Technol.* **2005**, 39, 164–174.
- (2) Jang, M.; Czoschke, N. M.; Lee, S.; Kamens, R. M. Heterogeneous atmospheric organic aerosol production by acid-catalyzed particle-phase reactions. *Science* **2002**, 298, 814–817.
- (3) Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* **1994**, 28, 185–188.
- (4) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; Wiley: New York, 1998.

- (5) Pankow, J. F. An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* **1994**, 28, 189–193.
- (6) Barsanti, K. C.; Pankow, J. F. Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 2: Dialdehydes, methylglyoxal, and diketones, submitted for publication.
- (7) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.
- (8) *Chemical Thermodynamic and Energy Release Evaluation (CHETAH)*, version 7.3; ASTM International: West Conshohocken, PA, 2002.

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ES0512529