Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—2. Dialdehydes, methylglyoxal, and diketones

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Abstract

Predicting the formation of organic particulate matter (OPM) in the atmosphere by absorptive gas/particle partitioning requires a knowledge of the identities, atmospheric levels, and physical properties of all condensable species. Data from field and chamber experiments have shown that a portion of atmospheric OPM samples are comprised of products generated during oxidation of volatile organic compounds. It has been suggested that some of these initially formed oxidation products also contribute to the formation of atmospheric OPM via molecular-weight (MW) building "accretion reactions". The role of such reactions as well as a general theoretical approach for evaluating their thermodynamic relevance in regard to atmospheric OPM formation, have been discussed in prior work. This work utilizes that approach in considerations of accretion reactions of glyoxal, two other dialdehydes, methylglyoxal, and two diketones. The methods used to predict free energy of formation (ΔG_f°) values (and hence equilibrium constant (K) values) indicate that: (1) for 1,4-butanedial, 2,3-butanedione, and 2,5-hexanedione, the accretion reactions considered are not favorable; (2) for C_6 and higher dialdehydes, reaction by aldol condensation may contribute to atmospheric OPM formation under certain circumstances, if kinetically favorable; and (3) 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.
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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

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(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 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).
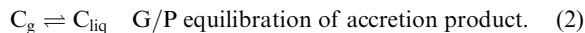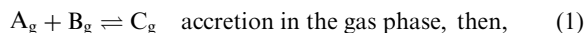
The original theory of absorptive G/P partitioning (Pankow, 1994a, b) explicitly allows that a portion of the absorptive fraction of an atmospheric PM sample can be comprised of organic constituents that are essentially "non-volatile". Haagen-Smit (1952) can be credited with the first recognition that 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[1] (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. Barsanti and Pankow (2004) proposed that the term "accretion reactions" be used in general discussions of MW-building reactions. (Simple oxidation reactions are excluded from the "accretion reaction" category (Barsanti and Pankow, 2004).) 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 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 (Barsanti and Pankow, 2004):

$$A_g + B_g \rightleftharpoons C_g \quad \text{accretion in the gas phase, then,} \quad (1)$$

$$C_g \rightleftharpoons C_{liq} \quad \text{G/P equilibration of accretion product.} \quad (2)$$

Barsanti and Pankow (2004) emphasized that 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 1 summarizes major types, formation reactions, and linkages of accretion products of proposed importance in the atmosphere. Barsanti and Pankow (2004) considered reactions of simple monoaldehydes and monoketones, and used thermodynamic considerations to show that: (1) neither hydration/polymerization nor hemiacetal/acetal formation are sufficiently thermodynamically favorable to require inclusion among accretion reactions considered important to OPM

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[1]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.