

Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions—Part 3: Carboxylic and dicarboxylic acids

Kelley C. Barsanti, James F. Pankow*

Department of Environmental and Biomolecular Systems, OGI School of Science & Engineering, Oregon Health & Science University, 20000 NW Walker Road, Beaverton, OR 97006, USA

Received 23 December 2005; accepted 12 March 2006

Abstract

The term “accretion reactions” has been used to describe the collection of reactions by which 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, 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]. Studies have shown that a significant fraction of atmospheric organic particulate matter (OPM) may be comprised of high-MW/low-volatility compounds [e.g., 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], which would be consistent with the occurrence of such accretion reactions in the atmosphere, [e.g., 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]. 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.

Barsanti and Pankow (2004, 2005) have developed and applied a general theoretical approach to evaluate the thermodynamic favorabilities of accretion reactions, including the extents to which they may be relevant for OPM formation in the atmosphere. That approach is applied here in the consideration of OPM formation by reactions of four mono- and dicarboxylic acids (acetic, malic, maleic, and pinic) to form esters and amides. It was concluded that for all of the acids considered, ester and amide formation are thermodynamically favored under the assumed conditions. 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.

© 2006 Published by Elsevier Ltd.

Keywords: Organic particulate matter; Secondary organic aerosol; SOA; Accretion reactions; Oligomers; Acids; Alcohols; Amides; Esters

*Corresponding author. Tel.: +1 503 690 1196.

E-mail address: pankow@ese.ogi.edu (J.F. Pankow).

1. Introduction

The molecular level characterization of the organic particulate matter (OPM) found in the atmosphere has proven difficult. Such OPM can be very complex, and at least part of that complexity is a result of the innumerable pathways by which organic compounds can react in the atmosphere. Volatile organic compounds (VOCs) can be oxidized to form multi-functional compounds, and 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 and thereby add molecular weight (MW), further decrease volatility, and thus increase their tendency to condense (Barsanti and Pankow, 2004, 2005). 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, loosely 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). Some studies have begun to consider the detection and quantification of oligomers per se, and the effects of particle acidity and parent-compound structure. These studies have shown that: (1) atmospherically relevant constituents (though not necessarily at atmospherically relevant levels) can 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 the 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 may be 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 may affect 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 with atmospherically relevant compounds. 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.

Barsanti and Pankow (2004, 2005) have developed and applied a general theoretical approach to evaluate the thermodynamic favorabilities of accretion reactions, including the extents to which they may be relevant for OPM formation in the atmosphere. In the consideration of C_4 – C_{10} aldehydes, ketones, dialdehydes, diketones, and methylglyoxal, it was concluded that: (1) hydration/oligomerization, hemiacetal/acetal formation, and aldol condensation are not favored for C_4 – C_{10} mono- and diketones, or for $\sim C_5$ 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 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.

This work applies the method of Barsanti and Pankow (2004) in the consideration of OPM formation by reaction of mono- and dicarboxylic acids to form esters and amides. The study compounds are acetic, malic, maleic, and pinic acid (Fig. 1). 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).

2. Overview of theoretical approach

2.1. Thermodynamic framework and mathematical solution process

The proposed mechanism by which oxidation products and other atmospheric constituents (e.g.,

Download English Version:

<https://daneshyari.com/en/article/4444005>

Download Persian Version:

<https://daneshyari.com/article/4444005>

[Daneshyari.com](https://daneshyari.com)