

Interactive comment on “Heterogeneous oxidation of saturated organic aerosols by hydroxyl radicals: Uptake kinetics and condensed-phase products” by I. J. George et al.

P. Ziemann (Referee)

paul.ziemann@ucr.edu

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I would like to add to this very interesting and important discussion of organic particle volatilization via heterogeneous oxidation by discussing a number of factors that can influence the volatilization process, including (1) organic molecular structure, (2) particle phase, (3) O₂ concentration, and (4) NO concentration. Some of these have been mentioned already, but not in a systematic way. These factors are first discussed with respect to radical-initiated oxidation of a linear, high molecular weight, liquid alkane (e.g., n-hexadecane [C₁₆]), used as a simple reference system to which other systems can then be compared. My hope is that this will make it easier to compare and explain

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results from the various systems being studied (now and in the future), based on current understanding of gas-phase and condensed-phase reaction mechanisms. It is still an open question as to how well this approach can be applied to interfacial and aerosol chemistry, but it is hoped that such comparisons will make the gaps in understanding more obvious and therefore help to focus future research.

It is generally agreed that the mechanism for the oxidation of saturated organic compounds by OH radicals (the mechanism should be similar for Cl and NO₃ radicals) involves H-atom abstraction followed by addition of O₂ to the alkyl radical to form an alkyl peroxy radical (RO₂). In the absence of NO, the RO₂ radicals can undergo a self-reaction to form either an alcohol + carbonyl pair (the Russell mechanism) or a pair of alkoxy radicals (RO), while in the presence of NO either an alkyl nitrate or an RO radical (+NO₂) is formed. The alkoxy radicals can (1) isomerize (leading to first-generation products such as 1,4-hydroxycarbonyls or 1,4-hydroxynitrates), (2) react with O₂ to form a carbonyl (+HO₂), or (3) decompose to a carbonyl and an alkyl radical. It is the latter pathway that can lead to volatilization, and thus factors that enhance the formation of alkoxy radicals and/or their decomposition should enhance volatilization. Given this basic framework and current understanding of gas-phase and liquid-phase chemistry, it is possible to evaluate the likely effects of variations in experimental conditions on particle volatilization.

1. Molecular structure: Results from gas-phase studies indicate that for carbon numbers larger than about C₆, decomposition of alkoxy radicals formed from n-alkanes is essentially zero (Aschmann et al. 2001). This is because the rate of 1,4-H-atom shift isomerization reactions are about two orders of magnitude faster than either the reaction with O₂ or decomposition for these alkoxy radicals (Atkinson, 1997a). One would therefore expect that for liquid, linear alkanes volatilization should be negligible (until enough functional groups have been added that the formation of beta-substituted alkoxy radicals becomes significant). In general, as the branching of the carbon chain increases, the yields of alkoxy radicals should increase, since tertiary RO₂ radicals do

not have H-atoms that can be transferred via the Russell mechanism. Alkoxy radical decomposition should also increase in importance relative to the competing reaction with O₂ and isomerization (Atkinson, 1997a).

2. Particle phase: Studies suggest that alkoxy radical formation from the self-reaction of primary or secondary RO₂ radicals is a minor pathway in liquids, and that the predominant products are the alcohol + carbonyl pair (Ingold, 1969 and reference therein). I am not aware of comparable studies carried out with solids. It is likely, however, that alkoxy radical decomposition and volatilization would be enhanced in solids since the isomerization pathway would be reduced and possibly eliminated.

3. O₂ concentration: The rate of the reaction of alkoxy radicals with O₂ (in s⁻¹ units) to form carbonyls depends linearly on the O₂ concentration, and for secondary alkoxy radicals formed from n-alkanes the rates of alkoxy radical decomposition and reaction with O₂ are approximately equal under atmospheric conditions (Atkinson, 1997a). Therefore, in systems where isomerization does not dominate the alkoxy radical chemistry, reducing the O₂ concentration below atmospheric levels should enhance alkoxy radical decomposition and volatilization.

4. NO concentration: The yields of alkoxy radicals from self-reactions of RO₂ radicals are in the range of 0.2-0.7 (Atkinson 1997b), and are at the upper end of this range or higher for the reactions of RO₂ radicals with NO. Therefore, increasing the NO concentration should probably enhance alkoxy radical formation and volatilization.

The behavior of the liquid n-hexadecane system can be compared, for example, with the systems that have been the focus of these discussions (George et al. 2007; Molina et al. 2004). For reference, a C₁₆ linear alkane has 28 secondary H-atoms and 6 primary H-atoms, which are less reactive than the secondary H-atoms.

The BEHS particles studied by George et al. (2007) are liquid, and BEHS is a C₂₆ branched diester. For the 50 H-atoms present in the molecule, 12 and 20 are primary and secondary H-atoms, respectively, comparable to those in hexadecane, 2 are ter-

tiary and thus have enhanced reactivity, and 16 are located adjacent to ethyl or ester groups. BEHS is therefore significantly more branched and functionalized than an n-alkane, which is likely to enhance volatilization via alkoxy radical decomposition. No information is provided on the O₂ concentration, so its effect cannot be evaluated, and the study was carried out in the absence of NO.

The alkane films and self-assembled alkyl monolayers studied by Molina et al. (2004) are both solid. The monolayers are made with C18 alkyl groups. The size of the alkanes in the films is not stated, but is probably about C20 or larger since they are solid. Neither of these systems contain branched species, and so would not be expected to volatilize if they were liquid (until reaction had added a substantial number of functional groups). Because the films are solid, however, thereby constraining isomerization, and the O₂ concentration (about 1 Torr or less) is more than two orders of magnitude below the atmospheric value, volatilization should be enhanced relative to a liquid n-alkane oxidized in air.

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Comments by Paul Ziemann

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