

Chemically diverse environmental interfaces and their reactions with ozone studied by sum frequency generation

Grace Y. Stokes, Avram M. Buchbinder, Julianne M. Gibbs-Davis, Karl A. Scheidt, Franz M. Geiger*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, United States

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ABSTRACT

Using tailor-made organic compounds tethered to solid substrates through organo-silane chemistry, we present a reductionist model study aimed at understanding the mechanisms of heterogeneous organic oxidation reactions at solid/air interfaces. The surface vibrational spectra of glass slides functionalized with the tropospherically relevant olefins 1-pentene, 2-hexene, cyclopentene, cyclohexene, and a menthenol derivative via aniline-silane linkers have been obtained through polarization-resolved broadband vibrational sum frequency generation (SFG). The olefinic and aliphatic CH stretches located above and below 3000 cm^{-1} , respectively, are clearly discernable and their spectral intensities are used to track, with 10 s time resolution, C=C double bond oxidation reactions of surface-bound cyclohexene at room temperature and with low ppm amounts of ozone at 1 atm. The olefinic CH stretching mode disappears at a rate of $0.05(1)\text{ s}^{-1}$, and the aliphatic asymmetric stretch modes increase at a rate of $0.04(1)\text{ s}^{-1}$. Analogous experiments show the formation of methyl groups even for those olefins under investigation that do not originally possess methyl groups. The implications for heterogeneous organic oxidation chemistry involving tropospheric dust particles are discussed.

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1. Introduction

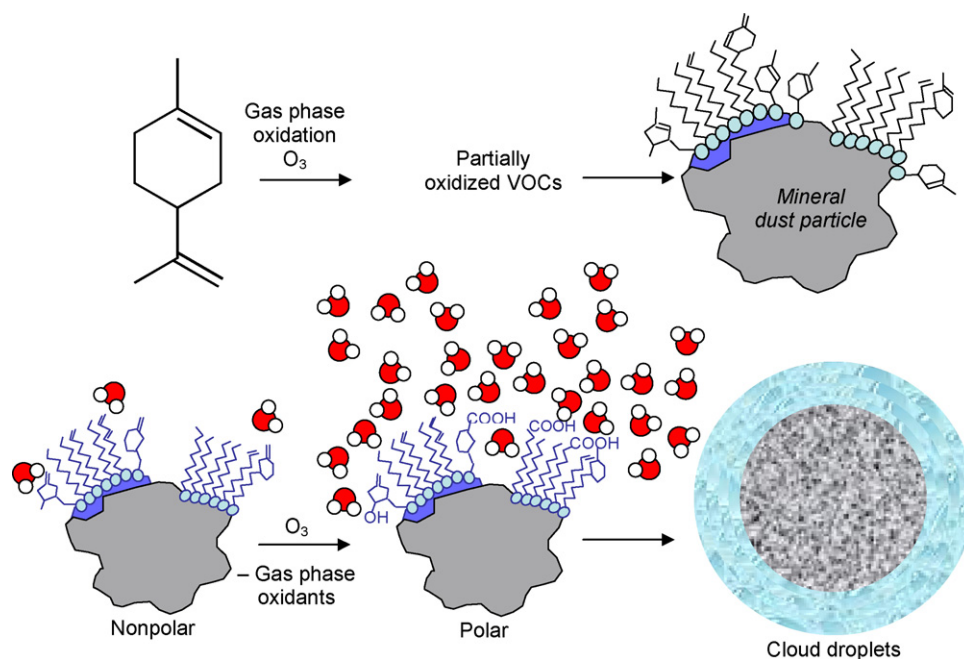
1.1. Heterogeneous atmospheric chemistry

The 2007 report from the Intergovernmental Panel on Climate Change states that “Anthropogenic contributions to aerosols (primarily sulfate, organic carbon, black carbon, nitrate, and dust) ... remain the dominant uncertainty in radiative forcing” [1] which is the net difference in incoming and outgoing solar radiation of the planet [2,3]. In general, a major challenge in reducing these uncertainties is rooted in a “low level of scientific understanding” [1] regarding the heterogeneous chemistry of atmospheric aerosols. Heterogeneous chemical processes involving atmospheric trace gases and aerosols include acid–base, redox, displacement, and radical reactions [2,3], and recent work has shown that including these types of heterogeneous processes in atmospheric models resolve discrepancies between measured ozone levels and those calculated using gas phase-only atmospheric models [4]. Multiphase chemistry is believed to be

important as well [5]. Nevertheless, mechanistic insight into most atmospherically relevant heterogeneous reactions is just beginning to emerge, but has not yet reached the high level of the scientific understanding established for homogeneous atmospheric reactions.

In this work, we will focus on unsaturated organic compounds that are common constituents of aerosols. We will characterize them using vibrational spectroscopy and study their heterogeneous oxidation reactions with ozone to understand the impact that aerosols have on climate and the chemical composition of the atmosphere [2,3,6–8]. Chemical analysis of atmospheric aerosols reveals that they often contain partially oxidized organic compounds [9,10]. These organic compounds can originate from gas phase oxidation reactions of unsaturated hydrocarbons that are produced by plants, i.e. terpenes, which are the dominant component of biogenic emissions [3,7–9,11,12]. Based on the importance of organic oxidation reactions in the gas phase [13–16], heterogeneous reactions between ozone and unsaturated organic compounds have been proposed to play a major role in tropospheric chemistry [6,8,17–19]. In general, it is thought that partially oxidized unsaturated organic compounds that are present in the lower atmosphere can bind to the surfaces of liquid and/or solid aerosols via their polar ends. Their remaining C=C double

* Corresponding author. Tel.: +1 847 467 6553; fax: +1 847 491 7713.
E-mail address: geigerf@chem.northwestern.edu (F.M. Geiger).



Scheme 1. Homogeneous and heterogeneous organic oxidation chemistry involving tropospheric ozone. Biogenic terpenes such as limonene are partially oxidized homogeneously and adsorb to mineral dust aerosol surfaces, where they are further oxidized heterogeneously. The resulting polar aerosol surface attracts atmospheric water vapor molecules, a cloud condensation nucleus forms, and the likelihood of cloud formation increases.

bonds should be exposed to the gas phase (see Scheme 1) [2] and subsequent reactions with ozone should occur. These heterogeneous processes are believed to switch the polarity of the hydrocarbon coating on the aerosol. This switch in polarity is thought to attract water molecules from the gas phase, forming a cloud condensation nucleus and increasing the likelihood of cloud formation. Due to the fact that clouds scatter solar radiation and energy quite differently from atmospheric gases [2,20], fundamental studies on heterogeneous organic oxidation chemistry should significantly improve our quantitative understanding of the Earth's energy balance and therefore reduce the uncertainties in predicting climate change.

1.2. Laboratory studies, challenges, and our approach

Previous laboratory studies addressing heterogeneous organic oxidation chemistry of atmospheric relevance have predominantly focused on straight chain alkenes and lipids such as oleic acid [6,21–35] and have not examined cyclic systems except for our previous work [36]. We note that even on high-dielectric substrates such as germanium or silicon, or metals such as gold, the characterization of organic monolayers on surfaces with vibrational spectroscopy is challenging due to image dipole formation, selection rules, and sensitivity. These challenges currently pose limits for determining the molecular orientation of adsorbates at interfaces and for tracking heterogeneous organic oxidation reactions in real time. As a result, the timescales and mechanisms of the heterogeneous reactions are not confidently established for terpenes.

Nonlinear optical spectroscopies complement existing laboratory experiments and yield molecular-level information that has already improved our understanding of heterogeneous organic oxidation reactions [36,37]. The heterogeneous processes are easily monitored with molecular specificity, directly at interfaces, in real time, under tropospherically representative reactant partial pressures and total pressure, and with exquisite sensitivity towards molecular orientation. In addition to their relevance in atmospheric chemistry, reactions of organic adlayers on metals

and metal oxides are important in heterogeneous catalysis [38–40]. Pioneering surface spectroscopy experiments relevant to heterogeneous catalysis have been conducted by Somorjai and coworkers [41–53], Campbell and coworkers [54–64], and Nuzzo and coworkers [65]. To obtain spectroscopic information on the reactant prior to the formation of metal–carbon bonds, the metal surfaces have to be cooled to cryogenic temperatures [66]. Unlike metals, glass surfaces can be functionalized and studied at room temperature with vibrational surface spectroscopy techniques such as sum frequency generation (SFG) without exhibiting back-bonding [67] and image dipoles [68].

Our interdisciplinary approach integrates the study of surface phenomena with synthetic chemistry to generate a variety of robust heterogeneous systems with tunable chemical and physical properties applicable to both catalysis and atmospheric chemistry. We generate chemically diverse tailor-made organic surfaces and track – in real time and at a total pressure of 1 atm – heterogeneous C=C double bond oxidation reactions of surface-bound olefins that are in contact with tropospherically relevant amounts of ozone. Glass surfaces in our study serve as proxies for the surfaces of mineral dust because the chemical composition of mineral dust aerosols reveals a high abundance of SiO₂ [69,70] and, as we described above, because mineral dust aerosols are now believed to influence tropospheric chemistry through surface reactions that involve adlayers of partially oxidized volatile organic compounds [3,5,71–73]. Thus, by using tailored organic compounds tethered to solid glass substrates, we present a reductionist model study aimed at understanding the mechanisms of atmospherically important heterogeneous organic oxidation reactions. Our use of organosilane chemistry allows us to analyze the kinetic data presented here in terms of C=C double bond oxidation reactions without interference from surface evaporation of the hydrocarbons, which tend to have high vapor pressures, or from bulk chemistry present in liquids. The approach simplifies chemical balancing and allows identification of the surface-bound reactants and products.

Our strategy also generates chemical diversity at interfaces for simulating a wide variety of surface-active organic compounds

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