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Atmospheric Heterogeneous Stereochemistry

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Abstract: While many biogenic and anthropogenic organic constituents in the atmosphere are surface-active and chiral, the role of stereochemistry in heterogeneous oxidation chemistry in the atmosphere has not yet been evaluated. Here, we present nonlinear vibrational surface spectra of fused silica substrates functionalized with quinuclidine diastereomers during exposure to 10^{11} to 10^{13} molecules of ozone per cm^3 in 1 atm helium to model ozone-limited and ozone-rich tropospheric conditions. Kinetic studies show that diastereomers that orient their reactive C=C double bonds toward the gas phase exhibit heterogeneous ozonolysis rate constants that are 2 times faster than diastereomers that orient their C=C double bonds away from the gas phase. Insofar as our laboratory model studies are representative of real world environments, our studies suggest that the propensity of aerosol particles coated with chiral semivolatile organic compounds to react with ozone may depend on stereochemistry. We expect that the differences in chemical accessibility will lead to the enrichment of one oxidation product stereoisomer over the other. The oxidation products could be gaseous or surface-bound, indicating that kinetic resolution could lead to the stereochemical enrichment of the gas phase or the aerosol, which may have also been important in prebiotic chemistry. Implications of these results for chiral markers that would allow for source appointments of anthropogenic versus biogenic carbon emissions are discussed.

Introduction

Organic compounds are ubiquitous in the atmosphere and play major roles in the formation, chemical transformation, and optical properties of aerosols.[1,2] While the molecular level understanding of atmospheric heterogeneous chemistry that has emerged over the past 2 decades is very high,[3−6] the role of heterogeneous atmospheric stereochemistry has not yet been evaluated. Ozone is achiral, and two mirror images of ozone on an achiral surface are fully superimposable. This situation may change for surfaces containing chiral olefins, and we evaluate it here for a model system that is relevant for understanding organic oxidation chemistry in the atmosphere. Given the fact that many biogenic and anthropogenic organic constituents in the atmosphere are chiral,[7] it is the purpose of this work to determine whether the heterogeneous oxidation of C=C double bonds is controlled by stereochemistry when olefin diastereomers are exposed to tropospherically relevant ozone levels at a total pressure of 1 atm. Surface-bound diastereomers adsorbed such that the reactive C=C double bonds are oriented toward the gas phase should exhibit faster ozonolysis rate constants than diastereomers that are adsorbed such that their C=C double bonds are oriented away from the gas phase. Here, we test this hypothesis by combining coherent interface-specific vibrational probes that are uniquely sensitive to molecular structure with synthetic methods that afford the preparation of surfaces functionalized with selected diastereomers.

The laboratory model studies presented here focus on the ozonolysis of C=C double bonds because they are commonly found within biosurfactants, which are important in marine aerosol chemistry,[8] as well as terpenes,[9] a key class of biogenic atmospheric constituents that are readily rendered surface-active via gas-phase oxidation.[10] At aerosol surfaces, the C=C double bonds are available for further heterogeneous reactions by atmospheric oxidants such as ozone. Laboratory model studies show that the impact of heterogeneous C=C double-bond oxidation processes on atmospheric chemistry includes changes in its chemical composition and in the propensity of aerosols to act as cloud condensation nuclei.[8,10−36] Specifically, atmo-

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spherically important gas-phase species such as formaldehyde and carbon dioxide have been detected as product species. Furthermore, the heterogeneous ozonolysis of C=C double bonds has been reported to follow a Langmuir−Hinshelwood mechanism.[8,37] Finally, depending on the ozone partial pressure, more or fewer polar surface-bound product species have been reported to form, which results in the formation of more or fewer hydrophobic ozone-processed surfaces.[38]

Given the atmospheric importance of heterogeneous organic oxidation processes, and given the ubiquity of chirality in nature, we determined the ozonolysis rates of two olefin diastereomers, each containing terminal C=C double bonds which are steered toward and away from the gas phase by the use of a quinuclidine group covalently bound to a fused silica surface (Figure 1A). A mere displacement of the C=C double bond from a terminal position toward an embedded position within the alkyl chain would not achieve the same effect as the one made possible by using the quinuclidine ring because terminal C=C double bonds are vastly more reactive than nonterminal double bonds.[7]

Experimental Approach

The surfaces are prepared by covalently linking (2*S*,4*S*,5*R*)-5-vinyl-2-quinuclidinecarboxaldehyde (CAS#66140-82-7) and (2*R*,4*S*,5*R*)-5-vinyl-2-quinuclidine carboxaldehyde (CAS# 66140-84-9) to aniline-functionalized fused silica substrates (see Supporting Information). After rinsing and sonication in absolute ethanol and then methylene chloride (Mallinckrodt) for 5 min, the substrates are dried under nitrogen. They were then studied using N(1s) XPS measurements (please see Supporting Information) to determine the relative surface coverages for the 2*R*- and 2*S*-diastereomers, which are found to be 51 ± 5% and 36 ± 5%, respectively (Figure 1B).

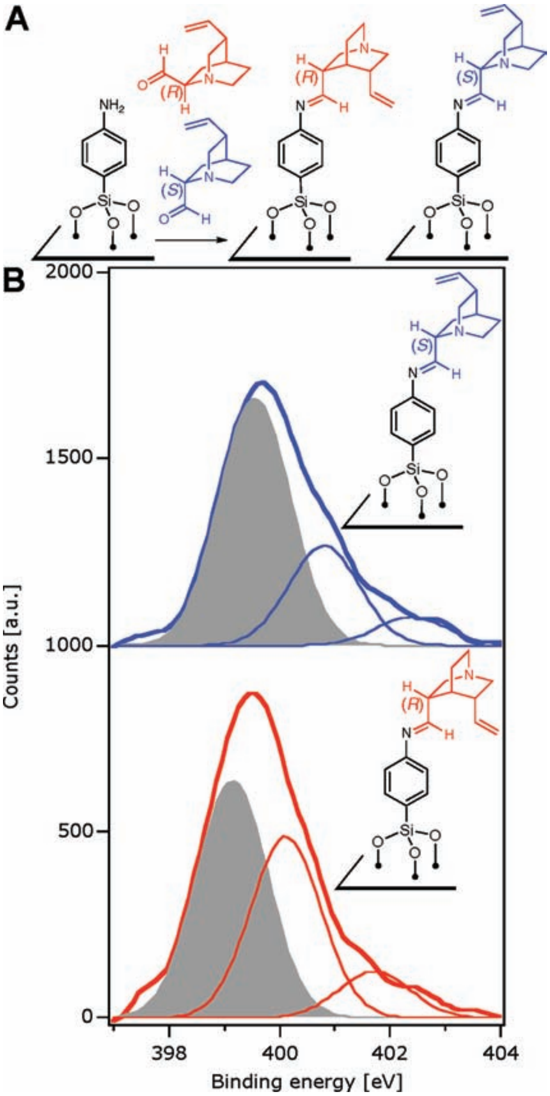

Figure 1. (A) Coupling of (2*S*,4*S*,5*R*)-5-vinyl-2-quinuclidine carboxaldehyde and (2*R*,4*S*,5*R*)-5-vinyl-2-quinuclidine carboxaldehyde to aniline silane-functionalized fused silica substrates. (B) N(1s) XPS spectra of fused silica substrates functionalized with the 2*S*- and the 2*R*-diastereomers (top and bottom, respectively). Gray areas and thin lines indicate the N(1s) XPS response of the unreacted aniline, the amide, and the quinuclidine groups. See text for details.

Using a previously described[39,40] laser system suitable for carrying out broadband vibrational sum frequency generation (SFG) studies, we identified the surface-bound diastereomers (Figure 2A,B) in the CH stretching region. The olefinic CH stretches of the terminal C=C double bond are clearly observable above 3000 cm^{-1} in both diastereomers when we interrogate the surface with a polarization combination that probes vibrational transitions oriented

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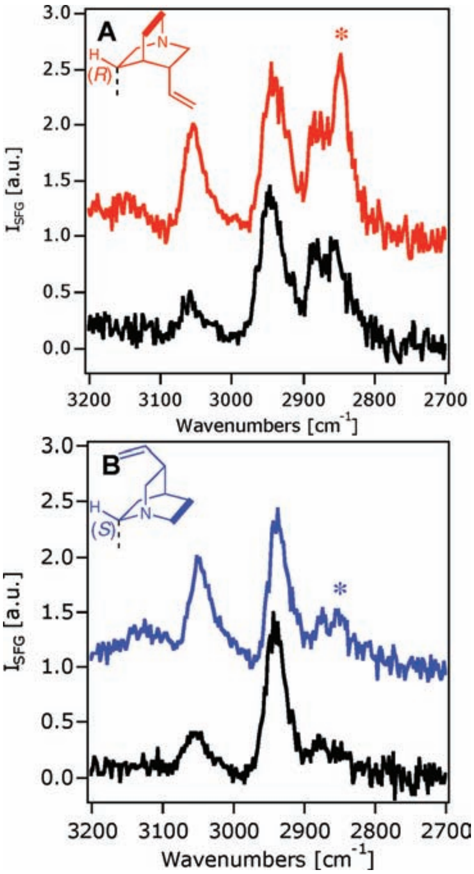

Figure 2. (A) ssp-Polarized vibrational sum frequency generation spectra of fused silica substrates functionalized with the 2*R*-diastereomer and the 2*S*-diastereomer before [red line (A); blue line (B)] and after [black line, (A) and (B)] exposure to 500 ppb of ozone in 1 atm helium. Please see text for details.

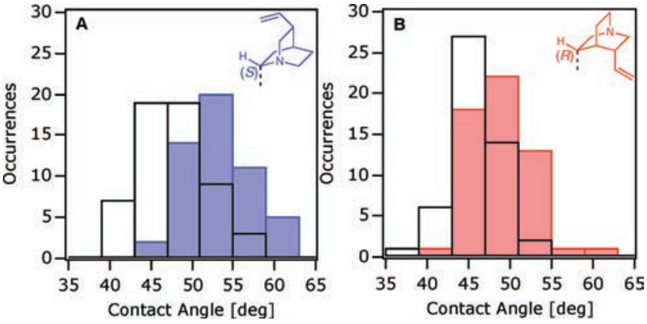

Figure 3. Contact angle measurement histograms of over 50 measurements each for fused silica substrates functionalized with the 2*S*- and the 2*R*-diastereomers before [blue and red histograms in (A) and (B), respectively] and after exposure to 350 ppb of ozone (empty boxes).

predominantly perpendicular to the surface.[41−45] In accordance with literature data,[46−50] the vibrational modes below 3000 cm^{-1} are assigned to the methylene asymmetric and symmetric CH stretches of the quinuclidine ring.

Parts (A) and (B) of Figure 2 probe the same number of vibrational modes because the SFG spectra are acquired using a polarization combination that probes achiral vibrational signatures and because the surface-bound diastereomers both have the same number of CH oscillators. However, (A) and (B) in Figure 2 also show that the SFG intensity attributed to the symmetric methylene stretch modes below 2900 cm^{-1} is much stronger in the 2*R*- than in the 2*S*-configured diastereomer, as indicated by the asterisks. This finding suggests that the ethyl bridge orientation in the 2*R*-diastereomer is orthogonal to the one in the 2*S*-diastereomer, as indicated by the thick single bonds in the Chemdraw structures. These results thus show how a subtle change in molecular orientation has a dramatic impact on the vibrational spectra, emphasizing the exquisite sensitivity of nonlinear vibrational spectroscopy to molecular structure. After characterizing the surfaces under investigation, we exposed the two surfaces to 500 ppb ozone by using a previously described Teflon gas flow chamber.[40,52]

Results and Discussion

Upon exposure to 500 ppb of ozone in 1 atm helium, the SFG spectra show a marked decrease in the SFG signal intensity attributed to the vinylic CH stretch at 3050 cm^{-1} (black traces in Figure 2A,B), indicating that ozonolysis has taken place. Simultaneous changes in the symmetric methylene CH stretch signatures of the ethyl bridge at 2850 cm^{-1} are quite pronounced in the 2*R*-diastereomer, which is consistent with the notion that its ethyl bridge reorients while ozone interacts with the quinuclidine ring to reach the buried C═C double bond. In contrast, the SFG spectra of the 2*S*-diastereomer exhibit little changes in the aliphatic CH stretch region, which suggests that little molecular rearrangement of the quinuclidine ring occurs upon ozone interaction. This interpretation supports the hypothesis that the C═C double bond of the 2*S*-diastereomer is readily accessible to gas-phase ozone.

Contact angle histograms (Figure 3A,B) show that exposing the 2*S*-diastereomer to 350 ppb of ozone results in 29 of 56 measurements with lower contact angles than those before ozone exposure, and that exposing the 2*R*-diastereomer to 350 ppb of ozone results in 15 of 52 measurements with lower contact angles than those before ozone exposure. These results are consistent with the formation of polar ozonolysis products at this ozone level. Similar to the finding by McArthur et al. that saturated siloxanes chemisorbed to silica are not degraded by ozone unless oxygen and UV light are present simultaneously,[51] we find that cyclohexane-functionalized surfaces yield no significant changes in the SFG signal intensities upon exposure to up to 1 ppm of ozone (see Supporting Information). This also indicates that the imine linkers are resilient to ozonolysis when using the low ozone partial pressures that are applied in this work.

After characterizing the olefin-functionalized surfaces before and after ozonolysis, we carried out kinetic measurements in which we tracked the SFG signal intensity from the olefinic CH stretches as a function of time while exposing the surfaces to 400 ppb of ozone (Figure 4A). These ozone-rich conditions are representative of highly polluted urban environments.[1,2] The

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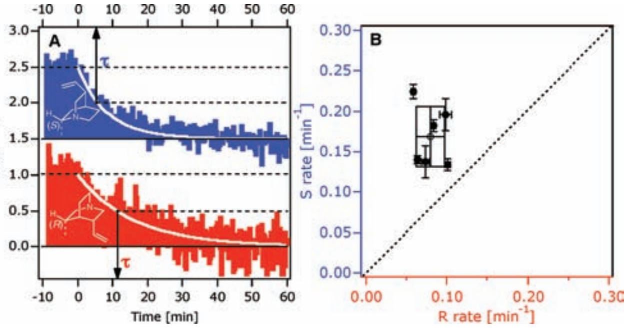

Figure 4. (A) SFG E-field vs time traces recorded at 3050 cm^{-1} of the 2*S*- and 2*R*-diastereomers upon exposure to 400 ppb of ozone (top and bottom, respectively). The white lines indicate the best fit to a first-order kinetic rate law, and the vertical arrows indicate the corresponding half-times. (B) Heterogeneous ozonolysis rates for the 2*S*-diastereomer plotted against that of the 2*R*-diastereomer. The dashed line indicates the result expected if there were no rate difference.

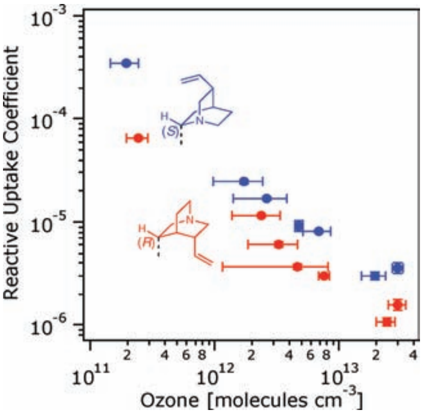

Figure 5. Reactive uptake coefficients (γ values) as a function of ozone concentration for the 2*R*- and 2*S*-diastereomers, indicated by the red and blue filled circles, respectively. Uncertainties in the x values are due to error (signal/noise and drift) in the UV−vis spectrometer, and uncertainties in the y values come from propagation of error of the first-order exponential fit of the decay in ESFG.

change in the SFG E-field versus time trace for the 2*R*-diastereomer was increased by 13% and then renormalized to the $t = 0$ level to account for its larger surface coverage when compared to the 2*S*-diastereomer.

Figure 4A shows that the 2*S*-diastereomer reacts faster than the 2*R*-diastereomer. Fitting the kinetic traces to a first-order rate law yields ozonolysis rates of 0.118 ± 0.004 min^{-1} and 0.063 ± 0.003 min^{-1} for the 2*S*-diastereomer and 2*R*-diastereomer, respectively. Repeating our kinetic studies for various ozone levels ranging from 10 ppb to 1 ppm (Figure 4B), we find that the ozonolysis rate of the 2*S*-diastereomer is consistently twice as high as the ozonolysis rate of the 2*R*-diastereomer. It is important to note that the SFG E-field does not only depend on the number density of oscillators located at the interface but also on their molecular orientation. Yet, on the basis of detailed polarization-resolved SFG studies for related olefin species before and after ozonolysis,[1] we attribute the SFG E-field change to C═C double-bond ozonolysis.

Following Finlayson-Pitts and co-workers,[17] Thornberry and Abbatt,[25] and our earlier work,[39,52] we calculated reactive uptake coefficients (γ values) for the heterogeneous ozonolysis reactions. Figure 5 shows higher γ values for the 2*S*-diastereomer than for the 2*R*-diastereomer at comparable ozone concentrations between 10 ppb and 1 ppm. By fitting the γ values to an expression that assumes a Langmuir−Hinshelwood mechanism,[17] we obtain second-order reaction rate constants that differ by a factor of 2 for the two diastereomers ($6.4(2) \times 10^{-18}$ cm^2 molecule^{-1} s^{-1} for the 2*R*-diastereomer and $2.9(3) \times 10^{-18}$ cm^2 molecule^{-1} s^{-1} for the 2*S*-diastereomer).

The reaction rate constants reported here are somewhat smaller than that reported for terminal alkene-functionalized glass surfaces (2×10^{-17} cm^2 molecule^{-1} s^{-1}).[17] We also quantify the ratio of the ozone desorption to adsorption rate constants, which is the inverse of the Langmuir binding constant, and find it to be identical within error for both diastereomers ($4 \pm 3 \times 10^{11}$ molecules cm^{-3} and $1.3 \pm 4 \times 10^{11}$ molecules cm^{-3}). These values are about 10 times smaller than those reported for benzo-[a]pyrene (BaP)-coated soot,[21] 100 times smaller than the one reported for terminal alkene-functionalized glass surfaces,[17] and about 1000 to 10,000 times smaller than those reported for anthracene adsorbed on water,[22] indicating that ozone adsorbs more strongly to the diastereomer-functionalized surfaces and may have a longer residence time there than for any of the other substrates. Given the similarity of the inverse Langmuir binding constants, we conclude that gas-phase ozone molecules reside in the olefin adlayer for similar residence time durations for both the 2*R*- and 2*S*-diastereomers. Thus, the faster reactivity we observe for the *S* diastereomer is most likely due to the faster reaction rate constant as opposed to the nonreactive interactions between ozone and the surface.

Summary and Outlook

Given that many of the partially oxidized gas-phase products originating from terpene ozonolysis contain stereocenters, and given the fact that many uncatalyzed reactions common in organic C═C double bond oxidation produce diastereomers with high stereoselectivity,[53] atmospheric heterogeneous stereochemistry may be one of the keys necessary for understanding the product formation and branching ratios of organic oxidations. This is especially important when considering the *cis* and *trans* ylides formed during ozonolysis.[54] If the ozonolysis of terpene diastereomers were modulated—or even controlled—by the chemistry occurring at the stereogenic carbon centers, it would be conceivable that stereochemistry also plays a key role in heterogeneous ozonolysis. In this work, we have demonstrated that heterogeneous ozonolysis reaction parameters depend on stereochemistry when quinuclidine-based olefin diastereomers covalently coupled to fused silica substrates are exposed to tropospherically relevant ozone levels. For ozone-limited and ozone-rich conditions that mimic ambient ozone concentrations in remote continental environments and highly polluted metropolitan areas, which typically range from 10^{11} to 10^{13} molecules of ozone per cm^3, the Langmuir binding constants were found to be within experimental error for both diastereomers, indicating that the nonreactive interactions between the two diastereomers and ozone are very similar. In contrast, the heterogeneous ozonolysis rate constant for the (2*S*,4*S*,5*R*)-5-vinyl-2-quinuclidine-functionalized surface, which contains a

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C═C double bond that is directed toward the gas phase, is 2 times faster than that for the opposite diastereomer, which contains a C═C double bond that is directed away from the gas phase. Reactive uptake coefficients, which are commonly used in global circulation models, mirror these differences.

Insofar as our laboratory model studies are representative of real world environments, one could speculate that heterogeneous stereochemistry may be important for understanding the chemistry of the troposphere. Our results suggest that the propensity of an aerosol particle coated with a chiral semivolatile organic compound to react with ozone may depend on surface orientation, which could be governed by stereochemistry. We expect that the differences in chemical accessibility will lead to the enrichment of one oxidation product stereoisomer over the other. The oxidation products could be gaseous or surface-bound, indicating that kinetic resolution[55] could lead to the stereochemical enrichment of the gas phase or the aerosol.

The results presented here suggest the presence of a stereochemically specific set of reactivity parameters that may improve the quantification and prediction of organic oxidation processes in atmospheric chemistry models. The finding that the first model system examined exhibits a clear reactivity difference when two opposite diastereomers are studied encourages us to pursue this work with chiral tropospheric olefins such as the important classes of diterpenes and oligoterpenes. Given that 1*S*,5*S* α-pinene is more common in European pine trees than in North American pine trees, where the opposite 1*R*,5*R* α-pinene diastereomer is more common,[56] it may be conceivable that atmospheric heterogeneous stereochemistry could play a key role in the formation of clouds over Europe as opposed to clouds over North America. Field measurements focusing on atmospheric stereochemistry are vitally needed for quantitatively assessing this role.

Building upon this work is the potential use of chiral organic molecules as atmospheric markers for source appointment and distinguishing between anthropogenic and natural sources of organic carbon. For example, the enantiomerically pure partially oxidized terpenes released during forest fires may be distinguished from the volatile chiral oligomers released during the combustion of commodity chemicals with predetermined stereochemistry, such as syndiotactic polypropylene. Such a use of "chiral atmospheric markers" could complement the use of isotopic and other markers to aid regulatory agencies and policy makers in environmental stewardship. Our results are also applicable toward the investigations of prebiotic chemistry and the origin of life, which has been hypothesized to involve heterogeneous aerosol reactions.[57−59] Heterogeneous stereochemistry occurring at prebiotic aerosol surfaces could have led to the production of a chiral excess of water-soluble product species, each containing the same stereogenic carbon atoms. It would be instructive to study whether continuing reactions inside the bulk aerosol could have led to homochiral building blocks of life and resulted in the fact that all amino acids are left-handed.[60]

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Supporting Information Available: Information on the synthesis and surface functionalization methods used in this work and the analysis of the XPS measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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