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# Laboratory Measurements of the Heterogeneous Oxidation of Condensed-Phase Organic Molecular Makers for Meat Cooking Emissions

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Multiphase oxidation of trace organic constituents inside of complex atmospheric particles is not well understood. In this study, organic aerosol formed from flash-vaporized residual grease from meat cooking was exposed to atmospherically relevant ozone concentrations in a smog chamber for 4−6 h. Changes in particle composition were measured to determine reaction rates for important molecular markers used for source apportionment analysis (oleic acid, palmitoleic acid, and cholesterol). Results are also presented for palmitic and stearic acids and likely reaction products. To quantify oxidation rates over a range of atmospheric conditions, separate experiments were conducted at low and high relative humidity and using particles mixed with and without secondary organic aerosol. Although particle composition, relative humidity, and secondary organic aerosol all influence the reaction rates, the unsaturated compounds were rapidly oxidized in every experiment. At typical summertime conditions, palmitoleic acid, oleic acid and cholesterol are estimated to have a chemical lifetime of about one day. The experimentally determined reaction rates are used in conjunction with the chemical mass balance model to investigate the effects of aging on source apportionment estimates. The results highlight that assumptions regarding the photochemical stability of molecular markers can lead to substantial biases in predictions of receptor models.

## Introduction

Molecular markers are individual organic compounds that are used in conjunction with receptor models to determine the sources of organic aerosols. A key assumption underlying the approach is that these compounds are photochemically stable (*1*). The validity of this assumption is uncertain (*2*). There is no question that organic particulate matter is bombarded with oxidants and that collisions involving OH radicals and ozone appear to have a high probability of leading to a reaction (*2*). However, the multiphase oxidation of trace organic constituents inside of complex atmospheric particles is not well understood.

Numerous laboratory studies have shown that molecular markers can oxidize at atmospherically relevant rates (*3*). However, the vast majority of the laboratory data are for simple mixtures and particle composition can dramatically influence oxidation rates (*3*–*5*). Therefore, it is not clear that these data can be extrapolated to atmospheric aerosols, which contain hundreds or even thousands of different semivolatile and condensed compounds (*6*). The potential disconnect is illustrated by data for oleic acid. The oxidation rate of oleic acid in a single component particle implies an atmospheric lifetime of minutes (*7*), while its prevalence in field data suggest it may have a lifetime of days (*1, 2, 8*).

In this paper, we present laboratory measurements of the oxidation rate of key molecular markers for meat-cooking emissions. Meat cooking is thought to be a major source of organic aerosol in urban environments (*1, 9*). The experiments feature realistic particles exposed to atmospherically relevant ozone concentrations inside a smog chamber. Reaction rates for oleic acid, palmitoleic acid, and cholesterol were determined using a relative rate approach. The data were used in conjunction with the chemical mass balance model to investigate the effects of oxidation on source apportionment estimates.

## Experimental Methods

We conducted aerosol oxidation experiments in the 12 $m^3$ Carnegie Mellon University smog chamber. Aerosols were added by flash vaporizing residual meat grease at 425 °C. Residual grease is the grease left in a pan after frying hamburger meat. Meat cooking emissions are caused by vaporization or splattering of grease by hot surfaces (*10*); therefore, flash-vaporized residual grease should be a realistic surrogate for fresh organic aerosol emissions from meat cooking. The composition of the residual grease particles was comparable to hamburger cooking source profiles (*10, 11*).

Particles were exposed to atmospherically relevant ozone concentrations (50−100 ppbv) for 4−6 h; near the end of each experiment, ozone concentrations were increased to 1−2 ppmv to try to drive the reactions to completion. Gas-phase tracers (*n*-pentane, 1-butene, and propene) were also added to the chamber and their concentrations monitored. Experiments were conducted in the dark with 2-butanol added as an OH scavenger.

The changes in molecular composition of the condensed-phase organics were determined by collecting filter samples, which were solvent extracted and analyzed using gas chromatography mass spectrometry (*12*). The goal was not to comprehensively analyze the meat grease, but to determine the decay of key molecular markers in a realistic matrix. The data from the smog chamber experiments were analyzed using a relative-rate approach to determine effective reaction rate constants for each target species (*12, 13*).

To simulate a range of atmospheric conditions, we conducted experiments at "low" (10 ± 5%) and "high" (40−60%) relative humidity and with and without secondary organic aerosol (SOA) formed from the ozonolysis of $\beta$-caryophyllene. Initial aerosol concentrations in the smog chamber were high, 350−10 000 $\mu g\ m^{-3}$, to ensure there was adequate sample mass for organic analysis. In the SOA coating experiments, SOA increased the total particle mass by about 20%. Although we use the phrase "SOA coating," the actual structure of the particle is not known. For example, the SOA more likely forms a solution with the other organics rather than a separate phase. Additional details on the experimental methods are contained in the Supporting Information.

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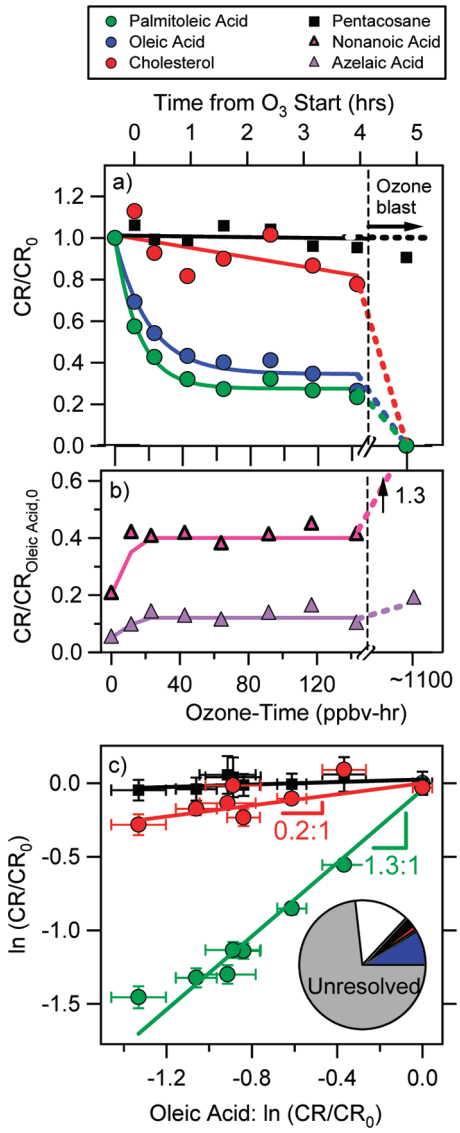


**FIGURE 1. Results from a typical oxidation experiment. Time series of (a) primary species and (b) oxidation products. (c) Condensed-phase relative rate plot with inset of meat grease composition. Data shown as concentration ratios (CR) with hexacosane to account for wall loss. The initial ozone concentration was 50 ppbv; during the "ozone blast" ozone concentrations were increased to 1.5 ppmv for the final 45 min of the experiment. Data in (a) are normalized by the initial CR of each species; data in (b) are normalized by the initial CR of oleic acid. In (c), the colored pieces in the pie chart correspond to the species shown in the legend, the white fraction is resolved compounds not included elsewhere in this figure (mostly palmitic and stearic acid), and the gray section is unresolved mass.**

## Results

Figure 1a plots time series of oleic acid, palmitoleic acid, cholesterol, and pentacosane concentration ratios with hexacosane measured in a typical oxidation experiment. The data are presented as concentration ratios with a nonreactive species to correct for wall losses (*12*). The initial ozone mixing ratio was 50 ppbv. Approximately 75% of the oleic and palmitoleic acid was oxidized in the first hour of the experiment, after which there was little change until exposure to ppmv levels of ozone at the end of the experiment. About 20% of the cholesterol was oxidized after 4 h of exposure to atmospherically relevant ozone levels.

Nonanoic and azelaic acid are known reaction products from ozonolysis of oleic acid (*4*). Figure 1b shows that the concentration ratios of nonanoic and azelaic acid increased throughout the experiment, mirroring the decay of the alkenoic acids. The production of these two acids in our experiments greatly exceed the 2−7% yields reported in the literature for oleic acid ozonolysis (*14*). A likely explanation is that there are many unsaturated acids in meat grease in addition to oleic acid (*10, 11*). For example, azelaic acid should also be formed from the ozonolysis of palmitoleic acid. Decanoic, octanoic, adipic, suberic, and succinic acids were also produced during the experiments.

Substantial decay of saturated acids such as palmitic and stearic acid can occur during ozonolysis of simple mixtures with oleic acid (*4, 5, 12*). This decay is attributed to secondary reactions involving the Criegee intermediate (*4*). In all of our experiments the concentration ratios of palmitic and stearic acid remained constant (not shown), which could be interpreted to mean that secondary chemistry is not important in complex particles. However, a more probable explanation is that the Criegee intermediates formed from the ozonolysis reactions are solvated by a large number of different compounds in our complex mixture. Therefore, the decay of any one species due to secondary chemistry was likely within the experimental error.

Figure 1a indicates that palmitoleic and oleic acids are initially oxidized at a very rapid rate followed by a period of significantly slower reaction; this change cannot be explained by the reduction in ozone concentrations. In contrast, cholesterol seemed to react at the more or less the same rate throughout the experiment. To try to drive the reactions to completion, 1−2 ppmv of ozone was added to the chamber for about the final hour of each experiment. In about one-third of the experiments the reactions were driven to completion (e.g., Figure 1a); in the other experiments some residual palmitoleic acid, oleic acid, and cholesterol was measured even after exposure to high ozone concentrations, ranging from 10−40% of the initial concentrations. The total integrated ozone exposure over the course of an experiment was 1100−2400 ppbv-hr, which is equivalent to one to two days of exposure to average summertime ozone levels.

**Relative Rate Analysis.** To compare reaction rates of different species we constructed ratio−ratio plots. Figure 1c shows such a plot based on the data presented in Figure 1a. It compares the reaction rate of palmitoleic acid, cholesterol, and pentacosane to oleic acid. The initial composition of the particles is indicated by the points in the upper right-hand corner of the plot. Oxidation decreases the concentration ratios, causing the data to shift toward the left and downward in a ratio−ratio plot.

The slopes of a ratio−ratio plot quantify the reaction rates of the different species relative to a reference species (eq S.1 in the Supporting Information) (*12, 13*). A slope less than one indicates the target species reacts slower than the reference species. For example, in the experiment shown in Figure 1, cholesterol reacted about 80% slower than oleic acid and palmitoleic acid reacted about 30% faster than oleic acid. For a nonreactive species such as pentacosane, the slope on a ratio−ratio plot is zero.

Data from all of the experiments are compiled in the ratio−ratio plots shown in Figure 2. First, we focus on comparing the relative reaction rates of different condensed phase species. Figures 2a compares the oxidation rate of palmitoleic acid to oleic acid. Almost all of the data are distributed along the same line, which means that there was little variability in the oxidation rate of palmitoleic acid relative to oleic acid. A linear regression of the complete data set yields a slope of 1.2, indicating that palmitoleic acid was oxidized, on average, 20% faster than oleic acid. Some of the

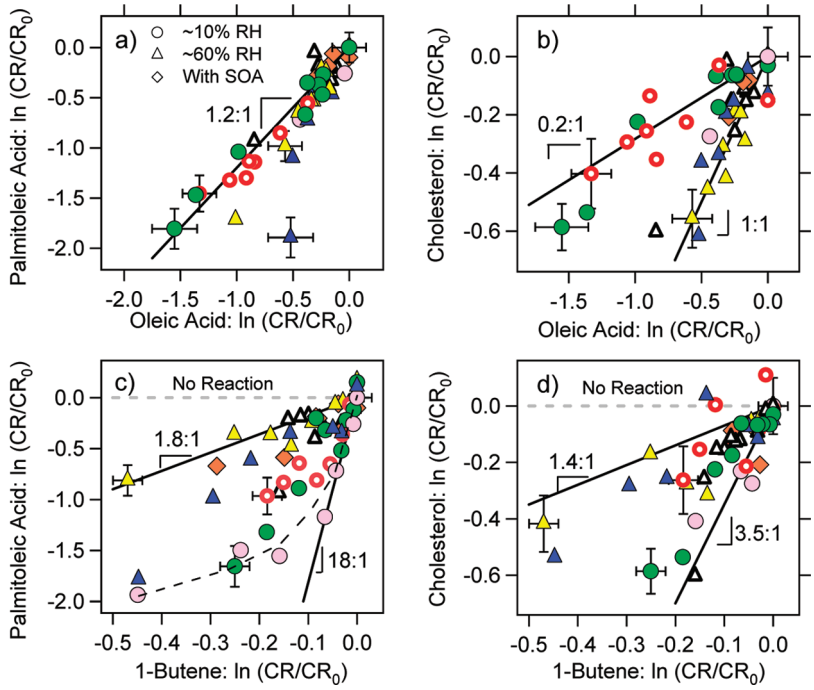


**FIGURE 2. Ratio-ratio plots compiling all experimental data. (a) palmitoleic acid versus oleic acid, (b) cholesterol versus oleic acid, (c) palmitoleic acid versus 1-butene, and (d) cholesterol versus 1-butene. Condensed phase data plotted as concentration ratios (CR) with hexacosane to account for wall loss. Symbols differentiate the experiment type: ○ = ~5–10% RH (3 separate experiments), Δ = ~40–60% RH (three separate experiments), ◊ = with condensed β-caryophyllene SOA (one experiment). Different shading/color indicates individual experiments. Solid lines in (c) and (d) are bounds on the ratios of reaction rates as discussed in the text. Error bars are shown on selected points to illustrate typical measurement uncertainty.**

data suggest a somewhat larger difference in the high RH experiments, but this is not a definitive conclusion.

Figure 2b compares the reaction rate of cholesterol to oleic acid. In this plot the data cluster into two groups, depending on experimental conditions. At high RH or with SOA coatings, cholesterol and oleic acid reacted at the same rate. (The SOA coating experiment was conducted at low RH). However, at low RH without SOA, cholesterol reacted 80% *slower* than oleic acid. Therefore, RH and SOA coatings have different effects on the oxidation kinetics of cholesterol versus alkenoic acids. This means that oleic acid cannot be considered a surrogate for all unsaturated species in heterogeneous oxidation studies.

The kinetic data can be better understood when viewed in a mixed-phase ratio-ratio plot (Figures 2c and 2d), which compares the reaction rate of a condensed-phase to a gas-phase species. A gas-phase species provides a consistent reference point because its rate constant does not vary during an experiment or from experiment to experiment. In every experiment, both alkenoic acids and cholesterol reacted faster than 1-butene. With few exceptions (discussed below), the data from each experiment organize along a straight line in a mixed phase ratio–ratio plot with the slope of the line varying depending on experimental conditions. These slopes indicate the effective rate constants of condensed-phase species (see eq S.2 in the Supporting Information), which depend on experimental conditions. High RH or SOA coatings decreased the effective rate constant of both alkenoic acids and cholesterol. Figure 2c indicates that the effective rate constants for palmitoleic acid decreased by about a factor of 10; for cholesterol it was about a factor of 2 (Figure 2d). Therefore, alkenoic acids were more sensitive to changes in experimental conditions than cholesterol and the variability shown in Figure 2b is mainly due to changes in the reaction rate of oleic acid and not cholesterol.

If a condensed-phase species effective rate constant changes during an experiment, then the data will be distributed along a curved as opposed to a straight line in a mixed-phase ratio–ratio plot (*12*). The best example of this is illustrated by the dashed line in Figure 2c; in this low RH experiment the effective rate constant of palmitoleic acid decreased by about a factor of 10 over the course of the experiment. A similar change was observed in one other low RH experiment (red circles in Figure 2c). However, all of the other mixed-phase relative data distribute along straight lines. Our data and those from previous studies suggest that large changes in effective rate constants only occur at large extents of reaction (*4, 5, 12, 15*).

Factors other than RH and SOA coating also appear to influence the reaction rates; for example, initial aerosol composition appears to be important. Although each experiment used the same residual grease sample, the initial mass fraction of oleic acid in the particles varied by about a factor of 10. This variability was caused by inadequate mixing of the stock grease sample prior to injection; more vigorous mixing performed in later experiments resulted in more consistent initial particle compositions. Comparing data across the set of experiments indicates that the cholesterol reaction rate appears to be somewhat correlated with the amount of alkenoic acids. As the relative concentration of alkenoic acids to cholesterol increases, the reaction rate for cholesterol increases. This dependence has also been observed in experiments with simple mixtures (*12*). Therefore, some of the variability shown in Figure 2 is likely due in part to differences in initial aerosol composition. Oleic acid typically contributed about 10% of the initial particle mass (Figure 1c); particles with substantially less oleic acid may have a different morphology or phase distribution (e.g., more solid than liquid) (*16*).

Since many gas-phase species have well-known kinetic data, the slopes of mixed-phase ratio–ratio plots such as those shown Figures 2c and 2d can be used to derive effective rate constants. Table 1 lists the upper and lower limits of the effective rate constants and e-fold lifetimes for cholesterol, palmitoleic acid, and oleic acid. These limits are based on the slopes of the two solid lines plotted in Figures 2c and 2d

**TABLE 1. Effective Ozonolysis Rate Constants and Lifetimes of Molecular Markers in Residual Meat Grease Aerosols**

| | effective rate constant ($ppbv^{-1}sec^{-1}$) | | lifetime[a] (days) | |
|---|---|---|---|---|
| compound | upper limit[b] | lower limit[c] | upper limit[b] | lower limit[c] |
| palmitoleic acid | $4.1 \times 10^{-6}$ | $4.1 \times 10^{-7}$ | 0.1 | 0.7 |
| oleic acid | $3.4 \times 10^{-6}$ | $2.9 \times 10^{-7}$ | 0.1 | 1.0 |
| cholesterol | $7.9 \times 10^{-7}$ | $3.2 \times 10^{-7}$ | 0.4 | 0.9 |

[a] e-fold lifetime calculated using 40 ppbv of ozone, average summertime concentrations. [b] Low relative humidity and no SOA. [c] High relative humidity or SOA.

and the published rate constant for 1-butene ($2.3 \times 10^{-7}$ $ppbv^{-1}sec^{-1}$ at 22 °C (*17*)). These lines bound the entire range of reaction rates measured at typical atmospheric ozone levels. In some experiments the oleic and palmitoleic acid effective rate constants decreased as the extent of reaction increased. These changes are contained within the limits listed in Table 1; however, an evolving effective rate constant means that the species does not have a single chemical lifetime.

## Discussion

The results in Figure 2 illustrate that RH, SOA, initial particle composition, and extent of reaction can all influence reaction kinetics. However, the data provide little insight into the underlying cause(s) of these changes. Oxidation of condensed-phase species by gas-phase oxidants is a complex process with possible rate-limiting steps related to oxidant uptake and solubility, species diffusion, and/or rate constant themselves (*18*). The rate constants listed in Table 1 are "effective" not true rate constants because they account for all of these phenomena (*12, 13*). Designing experiments to isolate these different processes is very challenging, especially with complex particles. Given the lack of data for atmospherically relevant systems, our goal was to obtain kinetic data for complex particles across a range of atmospheric conditions. These data help us assess the atmospheric significance of heterogeneous oxidation and identify problems for more detailed future study.

Given the inherent complexity of heterogeneous oxidation, many plausible hypotheses can be invoked to explain our data. We have discussed many of these in earlier work on simple mixtures (*12*). For example, the slowing of the oxidation rate of the alkenoic acids shown in Figure 1a could be due to depletion of these species near the particle surface. Since some of the effects are species dependent (e.g., RH and SOA coatings affect alkenoic acids and cholesterol differently), the changes cannot be solely due to changes in ozone solubility or other processes that affect all species equally.

Published kinetic data are available for some of the compounds investigated here. Most of the data are for oleic acid and almost all of the data are for simple mixtures (single compound or binary mixtures). Oleic acid in single component particles reacts very rapidly with ozone (atmospheric lifetime of minutes under summertime conditions), which is incongruous with the ubiquity of oleic acid in atmospheric samples (*7*). The oleic acid oxidation rates in the complex particles studied here are about 2 orders of magnitude slower than the pure particle data. Our most atmospherically relevant conditions (moderate RH or particles with SOA coatings) indicate an oleic acid lifetime of about one day, which is at least qualitatively consistent with ambient observations of oleic acid.

There is better agreement between our results and oleic acid kinetics measured in multicomponent particles. Experiments with actual meat cooking emissions suggest that some of the oleic acid has a half-life of minutes while the rest has a half-life of hours to days (*15*). Similar behavior has been observed in experiments with binary mixtures of oleic acid with an alkanoic acid and in somewhat more complex mixtures (*4, 5, 12*). We are not aware of any previous data that has investigated the effects of RH and SOA coatings on oxidation kinetics.

Our data do not answer the question of why oleic acid oxidation in complex particles is so much slower than in single component particles. Diffusion time scales in particles are estimated to be seconds to minutes (*2*); therefore, intraparticle mass transfer should not limit oxidation in our multihour experiments. In experiments with binary mixtures, the dramatic slowing of the oleic acid oxidation rate appears related to the formation of crystalline phases (*5*); however, crystalline phases are unlikely to form complex particles with hundreds of components (*19*). Decreased ozone solubility likely plays a role in the slower oxidation in complex particles.

An interesting question is whether or not some of the oleic acid becomes trapped inside the particles and therefore is effectively no longer available for reaction. This occurs in flow tube studies that expose particles to high ozone levels for short residence times (*5, 15*). A concern is that short residence times may limit the extent of reaction because of the coupling of mass transfer and chemistry in heterogeneous oxidation. Minor amounts of residual unsaturated species were observed in two-thirds of our experiments. However, our integrated ozone exposures (1100−2400 ppbv-hr) were not large enough to ensure complete reaction in every experiment based on the effective rate constants listed in Table 1. If some of the unsaturated species are trapped, our results and the rest of the published laboratory data suggest that it is minor fraction (in our experiments, residual concentrations were, on average, less than 20% of the initial concentrations). In every published study, the majority of the oleic acid has an atmospheric lifetime of about one day or less.

Our cholesterol data are in reasonable agreement with measurements of ozone uptake on pure cholesterol particles under dry conditions (*20*). The uptake data imply an e-fold lifetime of about 1 day at 40 ppbv of ozone, which is two times longer than our estimate for cholesterol in complex particles at the low RH (Table 1). A possible explanation for this difference is that pure cholesterol particles are solid under dry conditions, while adding impurities may create more liquid-like particles (*19*). Therefore, adding complexity may not always slow oxidation.

Figure 3 compares the new chamber results to ambient molecular marker data measured as part of the Pittsburgh Air Quality Study. The comparison is made using a ratio−ratio plot of palmitoleic and oleic acid concentrations normalized by stearic acid. The distribution of the ambient data along a diagonal line in this plot can be explained by oleic and palmitoleic acid being oxidized in atmospheric particles (*2*). However, mixing of emissions from different sources can also influence the organization of ambient data in a ratio−ratio plot (*2*).

The chamber data support the interpretation that alkenoic acids are being oxidized in atmospheric particles. First, the chamber data also organize along a diagonal line in Figure 3 because oleic and palmitoleic acid oxidize at basically the same rate while stearic acid does not react. The ambient alkenoic-acid-to-stearic-acid ratios vary by about a factor of 10. A similar spread can be created in as little as 6 hours of exposure of meat-grease particles to atmospherically relevant ozone concentrations. Therefore, the ambient data can be explained by atmospheric concentrations being dominated

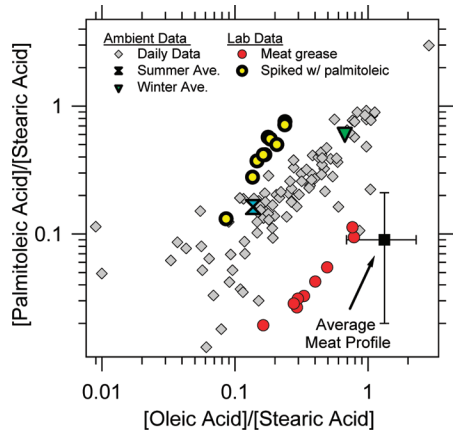


**FIGURE 3. Ratio−ratio plot comparing laboratory data for meat grease ozonolysis to ambient data from the Pittsburgh Air Quality Study. The "average meat profile" is the arithmetic average of nine published meat cooking source profiles with the error bars indicating the full range of published values (*10, 11, 24*).**

by fresh emissions on some days and by more aged emissions on others. Furthermore, ambient alkenoic-acid-to-stearic-acid ratios have a strong seasonal pattern that mirrors the changes in photochemical activity. The average wintertime ratio was about a factor 10 higher than the higher summertime ratio. A final piece of evidence that alkenoic acids are being oxidized in atmospheric particles is transport modeling studies that substantially overpredict summertime oleic acid concentrations (*8, 21*).

The only discrepancy between the ambient and chamber data shown in Figure 3 is that they have different oleic-to-palmitoleic-acid ratios. The unspiked chamber experiments have a ratio of about 10:1 versus about 1:1 in the ambient data. The ratio of the unspiked chamber data is consistent with published meat-cooking profiles (*10, 11*). In addition, almost all published source profiles are enriched in oleic acid relative to palmitoleic acid (*2, 9*). Therefore, the 1:1 oleic-to-palmitoleic-acid ratio in the ambient data is a puzzle. The data in this paper helps rules out the hypothesis that palmitoleic acid is being preferentially oxidized as the explanation for this discrepancy. The more likely explanation is some unidentified source that is enriched in palmitoleic acid (*2, 9*). This discrepancy is further discussed in Robinson et al. (*2, 9*) and is not unique to the Pittsburgh data set.

**Implications for Receptor Modeling.** To illustrate the atmospheric significance of the measured oxidation rates, Figure 4 plots the calculated decay of palmitoleic acid and cholesterol over a one-week period, which covers the range of ages of most particles in urban areas. The summertime calculations assume 40 ppbv of ozone, and results are presented for both the upper and lower rate constants listed in Table 1. The winter calculation assumes 10 ppbv of ozone and uses the slower reaction rate. The potential effects of trapping are illustrated by the light shaded region, which assumes that 20% of the initial mass of each compound is not oxidized.

Under summertime conditions, more than half of the alkenoic acids and cholesterol are predicted to oxidize in one day. In the winter more modest but still significant oxidation is predicted. Therefore, oxidation may dramatically reduce atmospheric concentrations of unsaturated molecular markers in areas strongly influenced by multiday regional pollution transport such as cities in the eastern United States. In the summertime, the measured oxidation rates are fast enough that concentrations of unsaturated markers in local emissions may be significantly affected.

The rapid oxidation shown in Figure 4 has important

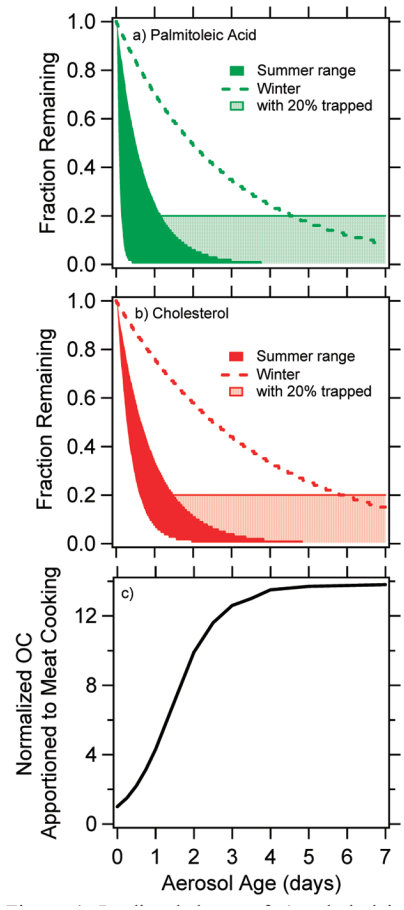


**FIGURE 4. Predicted decay of (a) palmitoleic acid and (b) cholesterol in meat grease particles exposed to typical summer (40 ppbv) and winter (10 ppbv) ozone concentrations. (c) Bias in ambient organic carbon apportioned by CMB to meat-cooking emissions as a function of mean aerosol under typical summertime conditions.**

implications for receptor modeling studies (*1, 9*). These studies often use different combinations of cholesterol, palmitoleic acid, and oleic acid to apportion ambient organic aerosol to meat cooking emissions; they also assume that these compounds are chemically stable (*1, 9*). To illustrate the potential effects of oxidation on source contribution estimates for meat cooking, chemical mass balance analysis was performed using the Pittsburgh Air Quality Study molecular marker data set (*9, 22*). We consider the two CMB models presented by Robinson et al. (*9*) that fit cholesterol and either palmitoleic or oleic acid to apportion meat cooking emissions. To simulate the effects of aging, we oxidized the oleic acid, palmitoleic acid, and cholesterol in the meat-cooking source profiles assuming a constant ozone concentration of 40 ppbv (the average summer concentration for Pittsburgh). We only considered oxidation at the slower rates listed in Table 1 given the ubiquity of SOA and the fact that RH in eastern United States is always greater than 10%. We also assumed that 20% of the unsaturated markers would not be oxidized.

Figure 4c presents the summertime average OC in Pittsburgh apportioned by CMB to meat cooking emissions as a function of mean age of the emissions. To quantify the bias due to aging, all of the CMB results have been normalized by the results from the traditional model (no oxidation). For example, a value of 2 indicates that the traditional CMB model apportions only half a s much OC to meat cooking as a model with aged profiles. In other words, oxidation causes the traditional CMB model to under-predict the contribution of meat cooking emissions by a factor of 2. A mean age of zero

indicates the results for the standard CMB model (no oxidation); a mean age of 1 day corresponds to the model in which the unsaturated marker concentrations in the meat cooking source profiles have been oxidized for 1 day assuming 40 ppbv of ozone.

Figure 4c reveals that oxidation of molecular markers can dramatically alter CMB source contribution estimates. For example, if unsaturated compounds in atmospheric particles are oxidized at the rates measured in this study, then one day of exposure to average summertime ozone concentrations will cause traditional CMB analysis to underestimate the contribution of meat cooking emissions by a factor of 4. Since some CMB models seem to apportion plausible amounts of organic aerosols to meat cooking emissions, this bias might seem unrealistically large. However, CMB results are strongly dependent on selection of fitting species and source profiles and some models only apportion a small fraction of ambient organic aerosols to cooking emissions (*9*). In addition, there may be important sources of unsaturated markers that are not accounted for in current receptor modeling studies (*23*).

The CMB results plotted in Figure 4c illustrate the large potential biases caused by oxidation, but they should not be used to quantitatively correct CMB results. First, the mean age of atmospheric particles is not known. Second, heterogeneous oxidation depends on atmospheric conditions such as relatively humidity and SOA coating, which requires aging calculations to track the atmospheric life of particles from each source. Finally, kinetic data are not available for the full range of atmospheric conditions. However, this and previous laboratory studies provide no basis to support the assumption that unsaturated molecular markers are stable. In particular this paper has shown that unsaturated species are rapidly oxidized in particles with complex, atmospherically relevant composition exposed to atmospherically relevant ozone concentrations. Therefore, future receptor modeling studies, especially those in areas influenced by regional transport, need to explicitly consider the effects of oxidation of oleic acid, palmitoleic acid and cholesterol. Although oxidation represents a substantial challenge to linear receptor models, the highly source specific nature of molecular markers mean that these compounds will remain an essential tool for source apportionment studies, but future studies must consider both mixing and oxidation as first-order processes.

## Acknowledgments

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## Supporting Information Available

Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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