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Exploring Heterogeneous Reactions of Model Lubricant Films with Indoor Oxidants: Products, Kinetics, and Energetics

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Research Progress

Background & Motivation. Most industrial lubricants are mixtures of hydrocarbons derived from crude oil, including paraffins (linear and branched hydrocarbons), naphthenes (cyclic hydrocarbons), and aromatic hydrocarbons.[1,2] Paraffinic lubricants are especially common in the automotive industry, and they can be further processed for other purposes; for example, many polyalphaolefin polymers, such as the plastics polyethylene and polypropylene, are derived from 1-decene in paraffinic base oils. Our research examines reactions that limit the lifetime of paraffinic lubricants, which we model with long-chain alkanes. Because indoor oxidation chemistry is dominated by reactions on surfaces,[3] we focus in particular on heterogeneous processes. Our overall objective is to explore multiphase reactions of alkane thin films with gas-phase oxidants to characterize the rates and mechanisms of lubricant aging.

Methods. Our initial work targeted the photo-oxidation of two long-chain, branched paraffins: squalene ($C_{30}H_{62}$, an unsaturated alkene) and pristane ($C_{19}H_{40}$, a saturated alkane). We used Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) to monitor multiphase reaction rates in real time, and we conducted analogous experiments in a flow tube for offline analysis with gas chromatography-mass spectrometry (GC-MS). Figure 1 shows the basic setup of our flow systems, modeled after work by Roberts et al.[4] and Schwartz-Narbonne et al.[5]

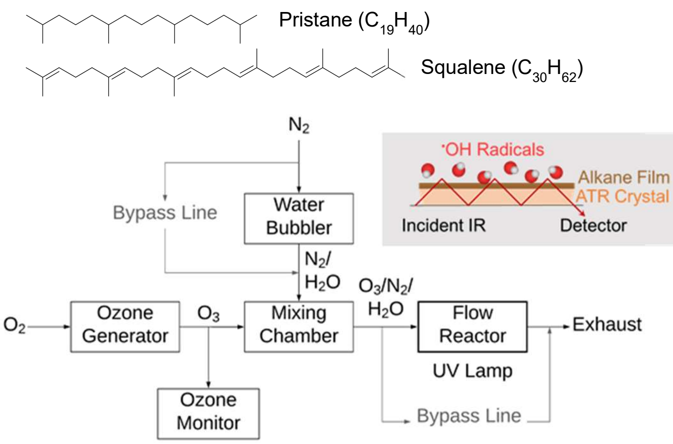

Fig 1. Flow assembly with ATR setup (inset). Adapted from references 4-5.

Preliminary Results. We began our work with oxidation of squalene by hydroxyl radicals (•OH), a well-studied model system,[6,7] to validate our approach. Figure 2 shows changes in the IR spectrum of a squalene film after exposure to high concentrations of •OH in the ATR reaction cell. As the reaction progresses, the peak near 1720 cm^{-1} appears as squalene is oxidized to form carbonyl-containing compounds. We are currently working to improve our sensitivity so that we can determine reaction rates under lower •OH exposure levels that are more relevant to indoor environments, and we will pursue product identification by GC-MS.

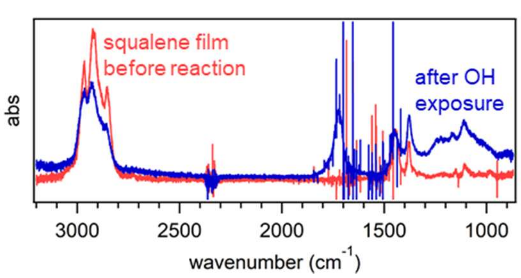

Fig 2. ATR spectra of squalene film before (red) and after (blue) exposure to hydroxyl radicals.

Meanwhile, separate experiments are underway to characterize reaction products of •OH-initiated photooxidation of pristane films. We detected several oxygenated products by GC-MS, as shown in the chromatogram in Figure 3a. In particular, we observed the functionalization of pristane to form various ketone (Figure 3b) and alcohol isomers, in agreement with known heterogeneous oxidation mechanisms.[8–10] However, we note that fragmentation in the mass spectrometer due to electron ionization precludes confident assignments of formulas and structures at this stage of the project. Our ongoing experiments seek to monitor the evolution of products by offline GC-MS analysis at timed intervals with internal standards to quantify reaction rates (Figure 3c). At the same time, we are continuing online measurements by ATR-FTIR for real-time, *in situ* determination of reaction rates.

Outlook. After refining our experimental methods, we plan to undertake a systematic study of multiphase oxidation of linear and branched hydrocarbons of varying chain length with and without lubricant stabilizers. Understanding gas–surface reactions of •OH with model paraffins will offer insight not only into lubricant stability, but also into the broader fundamental chemistry of heterogeneous oxidation reactions.

Impact on Career of PI

Support from ACS PRF has stimulated my research productivity as a brand new investigator while also bolstering my path toward tenure as an assistant professor at a small liberal arts college with an exclusively undergraduate student population. By combining my startup funds and internal support from the College of Wooster with the funding for students, supplies, and travel from PRF, I quickly expanded my research program beyond my initial plans: I was able to purchase sufficient supplies and hire enough students so that my lab could carry out two experiments in parallel on the same chemical system with complementary techniques. In addition, the funding for conference travel allowed me to present a poster at Pittcon for the first time in March 2019. Attending this conference was an important networking opportunity for me within the analytical chemistry community.

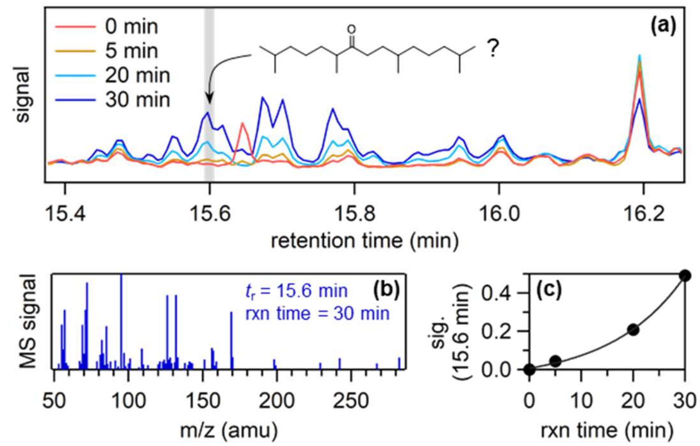

Fig 3. (a) Gas chromatogram of products formed when a pristane film is exposed to gas-phase hydroxyl radicals over a period of 30 minutes. (b) Mass spectrum of the shaded peak in the chromatogram, which may correspond to a ketone. (c) Exponential fit to the change in signal of the highlighted peak to model first-order kinetics.

Research and involvement in the scholarly community are two critical aspects of my evaluation for tenure. Indeed, receiving the grant was viewed favorably by the tenure committee and provost in my first biennial review. Moreover, the PRF UNI grant was my first grant as an independent investigator, and the feedback from reviewers helped me later when I crafted my own reviews for NOAA and NSF grants. In addition, I was able to mentor other faculty members at my institution and elsewhere who were preparing PRF proposals. Over the coming year, continued funding from PRF will enable me to take students to a national conference, which is viewed favorably for tenure, and to publish a peer-reviewed manuscript, which is a requirement for tenure.

Impact on Undergraduate Students

The College of Wooster has a robust program for undergraduate research in which every senior is required to write a complete research proposal, carry out independent experiments, present a public seminar and poster, write a thesis, and give an oral defense. However, internal funding for younger students is limited. The PRF grant has enabled me to start building continuity within a cohort of research students in my lab. Through combined support from PRF, my startup funds, and the College, five students have worked on PRF-related research over the 2018-2019 academic year and 2019 summer. These students include one first-generation college student, one female student, and two international students.

The hands-on experience the students gain in the research lab is invaluable for their development as skilled scientists and independent thinkers. My students not only learn to master flow assemblies, gas handling, ATR-FTIR, and GC-MS, they also grow in diverse areas such as data processing, data visualization, and oral and written communication. After successfully defending his thesis in spring 2019, the first PRF-supported student to graduate from my lab is now employed in soil testing for the oil and gas industry. To support my current students, I plan to use the travel budget during the 2019-2020 period to take a group of students to a national conference, likely the Fall 2020 ACS meeting. Presenting their research on a national stage is an important stepping stone in the students' professional development as they look toward future careers as scientists.

References

(1) Sequeira, A. *Lubricant Base Oil and Wax Processing*; Marcel Dekker: New York, 1994.
(2) Torbacke, M.; Rudolphi, A. K.; Kassfeldt, E. *Lubricants: Introduction to Properties and Performance*; Wiley: Chichester, UK, 2014.
(3) Weschler, C. J. *Indoor Air* **2011**, *21*, 205–218.
(4) Roberts, J. E.; Zeng, G.; Maron, M. K.; Mach, M.; Dwebi, I.; Liu, Y. *J. Chem. Educ.* **2016**, *93*, 733–737.
(5) Schwartz-Narbonne, H.; Wang, C.; Zhou, S.; Abbatt, J. P. D.; Faust, J. *Environ. Sci. Technol.* **2019**, *53*, 1217–1224.
(6) Nah, T.; Kessler, S. H.; Daumit, K. E.; Kroll, J. H.; Leone, S. R.; Wilson, K. R. *J. Phys. Chem. A* **2014**, *118*, 4106–4119.
(7) Lee, L.; Wilson, K. *J. Phys. Chem. A* **2016**, *120*, 6800–6812.
(8) Eliason, T. L.; Gilman, J. B.; Vaida, V. *Atmos. Environ.* **2004**, *38*, 1367–1378.
(9) George, I. J.; Abbatt, J. P. D. *Nat. Chem.* **2010**, *2*, 713–722.
(10) Ruehl, C. R.; Nah, T.; Isaacman, G.; Worton, D. R.; Chan, A. W. H.; Kolesar, K. R.; Cappa, C. D.; Goldstein, A. H.; Wilson, K. R. *J. Phys. Chem. A* **2013**, *117*, 3990–4000.