Measuring Heterogeneous Reaction Rates with ATR-FTIR Spectroscopy To Evaluate Chemical Fates in an Atmospheric Environment: A Physical Chemistry and Environmental Chemistry Laboratory Experiment

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S Supporting Information

ABSTRACT: This paper reports an undergraduate laboratory experiment to measure heterogeneous liquid/gas reaction kinetics (ozone-oleic acid and ozone-phenothrin) using a flow reactor coupled to an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer. The experiment is specially designed for an upper-level undergraduate Physical Chemistry laboratory course and may be incorporated in environmental chemistry and toxicology laboratory courses as well. From the experiment, students can measure heterogeneous reaction rates, calculate reactive uptake coefficients, and evaluate the lifetime of chemicals in an atmospheric environment, which is conducive to their understanding of several important concepts related to physical chemistry and environmental chemistry.

KEYWORDS: Upper-Division Undergraduate, Environmental Chemistry, Physical Chemistry, Laboratory Instruction, Interdisciplinary/Multidisciplinary, Atmospheric Chemistry, IR Spectroscopy, Fatty Acids, Kinetics, Quantitative Analysis
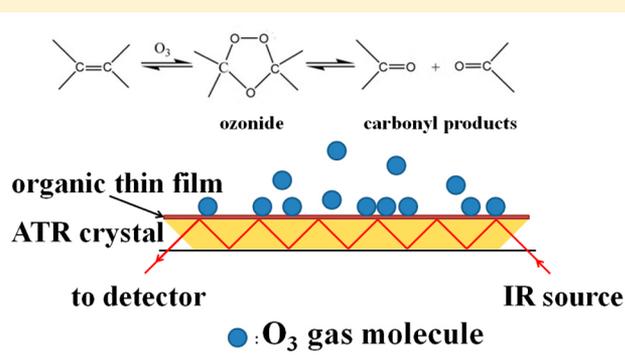
Chemical kinetics is an important branch of physical chemistry, and it deals with measurement of reaction rates in terms of reactant consumption or product formation with time. The study of reaction rates is critical, as it enables us to predict how fast a reaction mixture approaches equilibrium, understand how reaction conditions can be optimized to achieve desirable outcomes, and determine whether a reaction follows a sequence of elementary steps as described by the reaction mechanism. One extremely essential aspect of chemical kinetics, from both fundamental process and practical application perspectives, are heterogeneous reactions, where compositional changes in a chemical system take place at the gas—solid, gas—liquid, or liquid—solid interface. Despite their significance, experiments amenable to a simple heterogeneous kinetics study are often unavailable for an upper-level undergraduate physical chemical laboratory.[1] The lack of heterogeneous kinetics experiments in the undergraduate physical chemical laboratory is probably due to unavailability of expensive equipment and complexity of heterogeneous systems. For heterogeneous reaction kinetics measurements, experimental observations of surface-adsorbed species often entail sensitive techniques such as photoelectron spectroscopy, Auger electron spectroscopy, electron energy loss spectroscopy, thermal desorption mass spectrometry, etc., which are typically not available in undergraduate teaching laboratories. It has long been recognized that diffusion is an important step for heterogeneous reactions occurring at the surface of a liquid or solid; therefore, observed reaction kinetics are expected to be dependent on surface reactions and diffusion processes of the reactants. In the limit of very rapid surface reactions, the diffusion step may be rate limiting. On the other hand, in the limit of fast diffusion (e.g., gas phase diffusion), the surface reactions may be the rate-controlling step. It is also noted that the heterogeneous kinetics experiments reported in chemical education literature are usually limited to reactions between solid and liquid phases,[2,3] and gas/liquid or gas/solid reaction kinetics experiments, suitable for undergraduate physical chemistry laboratory course, are very scarce.

This paper describes a heterogeneous gas/liquid reaction kinetics experiment carried out by students in the Physical Chemistry Laboratory Course (CHEM4538) at the University of Colorado Denver using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. One advantage of the experiment is that it utilized the ATR-FTIR, an inexpensive equipment available in most chemistry teaching laboratories. Recently, the ATR-FTIR has also been demonstrated by Schuttlefield and Grassian[4,5] and Feng and Buhman,[6] as a highly versatile tool for undergraduate chemistry

laboratories (organic chemistry, inorganic chemistry, analytical chemistry, and physical chemistry) and undergraduate research. In the experiment, oxidation reaction between ozone and oleic acid (OA) liquid thin film were investigated to determine its reaction rate and probability. The reaction was chosen because of growing interest in this heterogeneous reaction on atmospheric organic aerosols. Organic matter in the atmosphere play crucial roles in various environmental issues, including air quality, sky visibility, public health, and climate change.[7−9] In the past decade, several long chain unsaturated fatty acids including oleic acid, linoleic acid, and linolenic acid have been used as proxies for unsaturated organic matter, and their interactions with ozone have been extensively studied for determination of reaction rate, mechanism and probability.[10−18] As the kinetics data of an ozone and OA reaction is relatively well established, this allows us to validate the experimental approach. To demonstrate that the method can also be applied to other heterogeneous reactions, we also measure kinetics of the ozone heterogeneous reaction with phenothrin, a major component of insecticides. The kinetics data of ozone reaction with phenothrin are reported for the first time, and expected to offer new insights into insecticides' fate and their impacts on air quality and public health.

A student who successfully completes this experimental exercise and accompanying laboratory is expected to achieve the following:

1. understand fundamental principles and concepts of chemical kinetics, heterogeneous reaction, and ATR-IR spectroscopy;
2. recognize significance of heterogeneous reactions in atmospheric environment;
3. demonstrate critical thinking in determination of reaction rate and probability for a heterogeneous reaction;
4. present experimental results in oral and written forms, adhering to proper chemical convection;
5. possess knowledge of safe laboratory practice and conduct themselves responsibly.

■ BACKGROUND

For reactions involving more than one reactant, finding an exact solution to a differential equation with two or more variables can become prohibitively difficult. For example, consider the following reaction:

$$A + B \xrightarrow{k} P \text{ (product)} \tag{1}$$

The second-order rate equation is expressed by

$$-\frac{d[A]}{dt} = k[A][B] \tag{2}$$

where k is the second-order rate constant, and $[A]$ and $[B]$ are the concentrations of reactants. If the experimental conditions are designed to be pseudo-first-order, i.e., $[B] \gg [A]$, then during the course of reaction, $[B]$ remains almost unchanged. As a result, the reaction is reduced to first order in the reactant, and eq 2 can be rewritten as

$$-\frac{d[A]}{dt} = k'[A] \tag{3}$$

where k' denotes the pseudo-first-order rate constant (also known as apparent rate constant) and it is equal to $k[B]$. Under the pseudo-first-order condition, concentrations of the reactant

A or the product P are expected to change exponentially with reaction time. Temperature dependent rate constants may be used to determine reaction activation energy based on the Arrhenius equation, where E_a is activation energy, R is gas constant, and A is pre-exponential factor. According to the eq 4, a plot of $\ln(k)$ versus $1/T$ gives a straight line and slope can be used to calculate activation energy.

$$-\ln(k) = \frac{-E_a}{RT} + \ln(A) \tag{4}$$

For gas−solid or gas−liquid heterogeneous reactions (for instance, O_3 with OA thin film), the reaction probability of the gaseous reactant (also called reactive uptake coefficient), which is defined as the ratio of the number of gaseous molecules removed by surface chemical reactions over the total number of gaseous molecules colliding at the surface,[7] can be calculated by the following equation[19]

$$\frac{d[OA]}{dt} = -\gamma \left(\frac{N_{O_3}\overline{C}}{4} \right) \frac{S_A}{V} \tag{5}$$

where $d[OA]/dt = -k'[OA]$, and $[OA]$ is the concentration of OA (molecules cm^{-3}); k' is the pseudo-first-order rate constant; $\overline{C}$ is the mean speed of ozone molecules in gas phase (cm s^{-1}); N is the concentration of O_3 (molecules cm^{-3}); S_A/V is the surface area-to-volume ratio of the OA thin film (cm^{-1}).

Residence time or lifetime of a substance tells us on average how long molecules of the substance will stay in the atmosphere before they are removed. On the basis of the heterogeneous reaction rate constant, the residence time of atmospheric organics resulting from the reaction with ozone may be estimated by the following equation:[8]

$$\tau = 1/k' \tag{6}$$

where τ is the residence time (s) and k' is pseudo-first-order rate constant.

■ EXPERIMENTS

The ATR-FTIR flow system (Figure 1) is similar to the one used in our recent studies.[16,20] Details about materials and equipment required in this experiment can be found in Supporting Information. The heterogeneous reaction of an OA
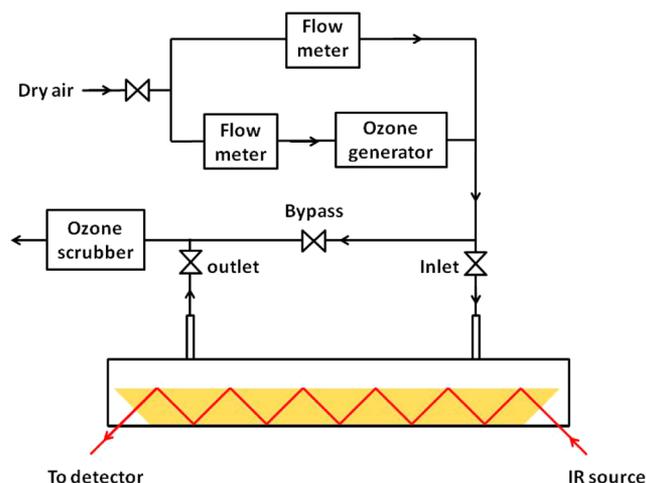
Figure 1. A schematic diagram of the ATR-FTIR flow system.

thin film with ozone was monitored in a real time fashion by an infrared spectrometer (Nicolet 6700) equipped with a multiple reflection ATR accessory (Harrick Scientific Horizon), a flow cell (Harrick Scientific HON-FLS) and a liquid-nitrogen cooled MCT detector. A ZnSe ATR crystal (refractive index: 2.4, 5 × 1 cm^2) was selected for its large penetration depth (~1.1 μm at 1700 cm^{-1}).[16,20] The OA thin film was made by adding a 100 μL solution of 3 mM oleic acid (99% purity, Acros Organics) in acetone (99% purity, Aldrich) directly onto the ZnSe crystal using a micropipette. The amount of OA and acetone was adequate to completely cover the whole ZnSe crystal surface (1 cm × 5 cm). The acetone usually evaporated entirely within 3 min, which can be corroborated by the IR spectra. The thin film thickness was estimated to be ~0.2 μm, much less than the penetration depth of evanescent wave, so that the bulk of the film could be completely probed by the IR beam.

Ozone was produced by flowing a small stream of dry air (50 mL/min) through a UV light source (Pen-Ray), and then diluted by a second flow of air of 950 mL/min. The flow rates were adjusted by two mass controllers. The ozone concentration were measured downstream with an ozone monitor (UV-100, Ozone solutions) and they were about (350 ± 10) ppb for oleic acid and about (230 ± 10) ppb for phenothrin. It is noted that it may take several minutes to produce an ozone flow with a steady concentration after the UV light source is turned on. To minimize the uncertainty resulting from the changing ozone concentration, an additional bypass line was added. Ozone flow was kept on throughout the experiments and was switched back and forth between the bypass line and the reaction line through the flow reactor.

The ozone flow was initially directed to the bypass line while obtaining the background spectrum of the clean ATR crystal. Once the acetone was no longer observed from the IR spectra, the OA thin film was ready for heterogeneous reaction. All experiments were conducted at room temperature (23 ± 1 °C) except for temperature dependent experiments, and all IR spectra were collected automatically using the macro function built in the OMNIC program in the range of 650−4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 32 scans.[16,20]

This experiment is suitable for a small group (2−3) of undergraduate students in a physical chemistry laboratory course. The heterogeneous reaction kinetics experiments usually take between 2 and 3 h. Recent studies[16,20] have shown that ozone initiated heterogeneous oxidation reactions of unsaturated fatty acids follow the Langmuir−Hinshelwood mechanism and pseudo-first-order rate constants display nearly linear dependence on ozone concentration up to ~50 ppm. As a result, for much slower reactions, the ozone concentration can be increased accordingly to ensure the experiments can still be completed within the allowed time. On the other hand, if time permits, the experiment can also be conducted under temperature controlled conditions, so that temperature dependent kinetics data can be obtained.

■ HAZARDS

Acetone is a flammable liquid, harmful if swallowed or inhaled, and can cause irritation to skin, eyes and respiratory tract. Phenothrin is harmful or fatal if swallowed and can cause irritation to skin, eyes, and the respiratory tract. Refer to the Material Safety Data Sheets for acetone and phenothrin. The ZnSe crystal should be handled with care.

■ RESULTS AND DISCUSSION

Oleic acid is an 18-carbon chain unsaturated carboxylic acid. Figure 2 presents an infrared spectrum of the fresh OA thin film
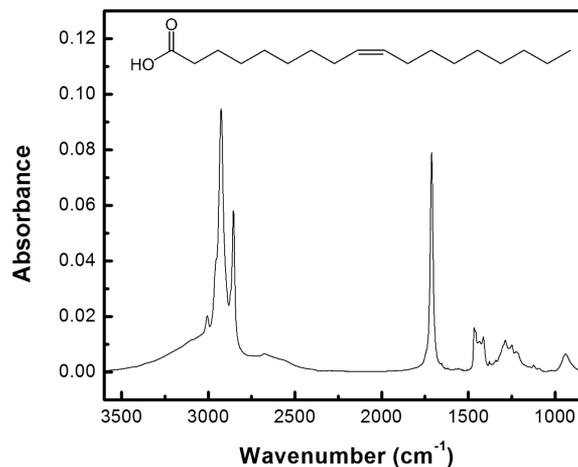

Figure 2. Students acquired FTIR spectrum of fresh oleic acid thin film at room temperature.

at room temperature. Generally, the main absorption features arise from −CH$_3$, −CH$_2$, and C=O groups. Assignments of infrared vibration modes of fresh OA and ozone exposed thin films are listed in Table 1.

Table 1. IR Feature Assignments of Fresh Oleic Acid and Ozone Reacted Thin Films

Wavenumber (cm^{-1})	Assignment
	Fresh Oleic Acid Thin Film
3006	=CH stretch
2925	−CH$_2$ antisymmetric stretching
2854	−CH$_2$ symmetric stretching
1710	carboxylic C=O stretching
1465	−CH$_2$ bending
1412	−CH$_2$ bending
1286	−CH$_2$ wagging
1249	−CH$_2$ wagging
1222	−CH$_2$ wagging
939	carboxylic −COH out-of-plane bending
	Ozone Reacted Thin Film
1743	ester C=O stretching
1710	ketones, aldehydes and carboxylic acids C=O stretching

Once the heterogeneous oxidation reaction takes place, it is expected to proceed following an ozonolysis mechanism (i.e., ozone attacks C=C double bond to form primary ozonides), followed by the formation of Criegee intermediates, which can further recombine with an aldehyde or ketone to form secondary ozonides or react with a carboxylic group, forming α-acyloxyalkyl hydroperoxide and cyclic diperoxides.[16,20] As shown in the inset of Figure 3, the C=O stretching band at 1710 cm^{-1}, which is reportedly attributable to ketone, aldehyde and carboxylic acid C=O stretching vibrations, decreased gradually as the heterogeneous reaction progressed.[16,20] Since the C=O oscillator strength in carboxylic acid is about 2 orders of magnitude higher than in ketones and aldehydes,[21,22] carboxylic acids are expected to dominate C=O absorption
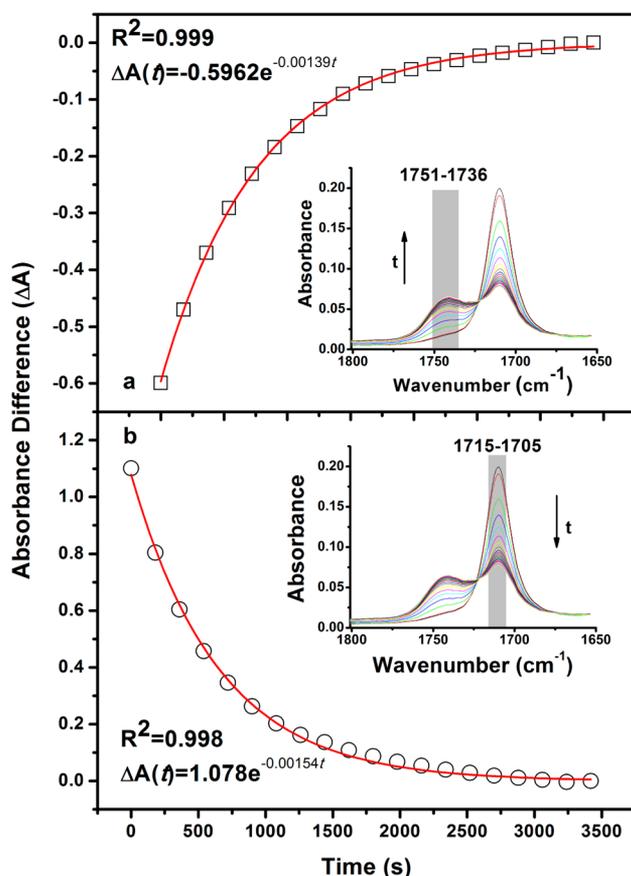
Figure 3. Students acquired exponential curve-fitting results of the absorbance difference in C=O stretching bands of OA thin film. Inset displays IR spectra evolution during the reaction.

behaviors near 1710 cm^{-1}. Accompanying with the decrease in absorption at 1710 cm^{-1}, a new band located at ∼1743 cm^{-1}, which is characteristic of an ester C=O absorption, appeared and increased gradually. Additionally, an isosbestic point near 1725 cm^{-1} was observed, an indicative of a transformation from an acid to an ester.[16,20]

With the temporal spectral changes in the two C=O bands (1710 and 1743 cm^{-1}), the kinetics of the heterogeneous reaction can be derived. On the basis of the Beer's law, absorbance values at ∼1710 and ∼1743 cm^{-1} are expected to be linearly proportional to the concentrations of reactant and product, respectively. In our experiment, ozone to OA molar ratio was kept at least 10 times at any given moment throughout the reaction to meet the pseudo-first-order condition. As such, the absorbance values of both C=O are expected to exhibit an exponential pattern over time. Figure 3 reveals the time dependent absorbance profiles of C=O (1743 and 1710 cm^{-1}), and their corresponding curve-fitting results. The exponential function fit the time dependent absorbance data strikingly well, and the pseudo-first-order rate constants k', based on C=O absorbance data at 1743 and 1710 cm^{-1}, are 1.54 × 10^{-3} and 1.39 × 10^{-3} s^{-1}, respectively. Such a good agreement implies that pseudo-first-order condition was met and secondary chemistry was negligible. With the k' value, ozone reaction probability (reactive uptake coefficient) γ was estimated as 8.0 × 10^{-4} using eq 4. This is in excellent agreement with literature values of (8.3 ± 0.2) × 10^{-4},[8] (8.0 ± 1.0) × 10^{-4},[11] and (7.9 ± 0.3) × 10^{-4},[12] all of which were obtained based on a thin film flow system coupled to a chemical

ionization mass spectrometer. In an urban setting, background ozone concentrations are typically around 20−45 ppb, but can be easily increased by 15−25 ppb as a result of a forest fire.[23] With that, the estimated residence time of oleic acid in the atmosphere before it is removed by ozone is about one and a half hours.

The experiment can also be carried out at different temperatures to obtain activation energy. Temperature control can be achieved by circulating water through a stainless steel block surrounding the flow reactor (Harrick Scientific #HON-FSS-TC3) or using a heated trough plate with a temperature controller (New Era #68205E-L-1 and #67002). Figure 1 in the Supporting Information displays the measured apparent rate constants as a function of temperature ranging from 288 to 304 K. A linear curve fitting according to the eq 4 gives activation energy of 4.3 ± 0.4 kJ/mol. The low activation energy may indicate that there is no energy barrier for the heterogeneous reaction of oleic acid and ozone. Such weak temperature dependence has also been reported in the studies of ozone reaction with other liquid samples including linoleic acid,[16] squalene,[24] 1-tridecene and canola oil.[25]

Figure 4 exhibits time dependent absorbance data of C=C−H and O=C−H deformation bands (854 and 937 cm^{-1}) in
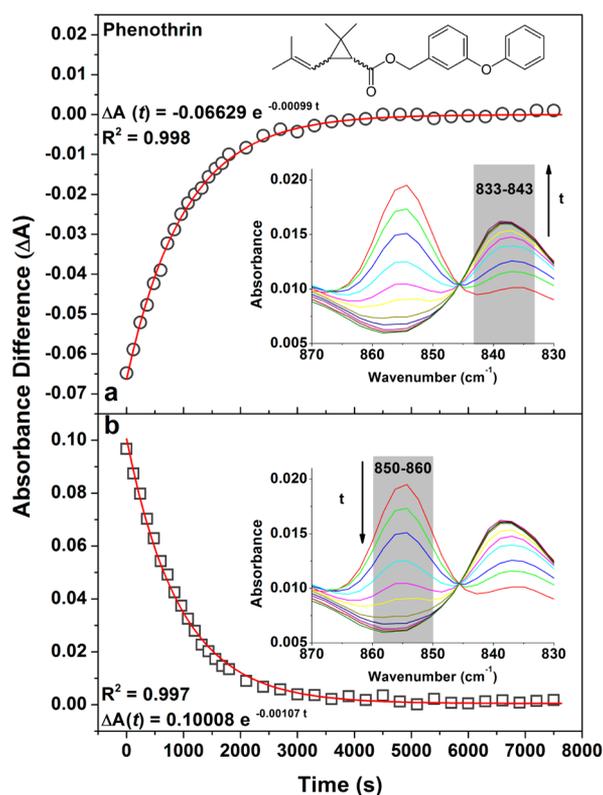

Figure 4. Students acquired exponential curve-fitting results of the absorbance difference in =C−H deformation bands of phenothrin thin film. Inset displays IR spectra evolution during the reaction.

phenothrin, and their curve-fitting results. Again, both curves present excellent exponential behaviors, and the pseudo-first-order rate constants are 1.07 × 10^{-3} and 9.90 × 10^{-4} s^{-1}. The calculated ozone reaction probability onto phenothrin surface is 4.6 × 10^{-4} and the estimated residence time of phenothrin is less than 2 h.

CONCLUSIONS

ATR-FTIR spectroscopy coupled with a flow cell is a simple, inexpensive method for heterogeneous reaction kinetics measurements. It is well-suited for an upper-level physical chemistry laboratory course in a small group setting. It may also be incorporated in other undergraduate laboratory courses such as environmental chemistry, toxicology, etc. and independent research project. From the experiment, students are introduced to several important concepts related to physical chemistry and environmental chemistry, including chemical kinetics, activation energy, heterogeneous reactions, pseudo-first-order approximation, Beer's law, reaction probability, and residence time.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00290.

Instructions to students (PDF, DOCX)
Instructor Notes (PDF, DOCX)
Recitation Note(PDF)
Supporting Information Figure 1 (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. *Experiments in Physical Chemistry*, 8th ed.; McGraw-Hill Higher Education, 2009.

(2) Gates, B. C.; Sherman, J. D. Experiments in Heterogeneous Catalysis: Kinetics of Alcohol Dehydration Reaction. *Chem. Eng. Educ.* **1975**, 124−127.

(3) Power, G. P.; Drok, K. J.; Ritchie, I. M. A Simple Electrochemical Approach to Heterogeneous Reaction Kinetics. *J. Chem. Educ.* **1998**, 75, 1145−1149.

(4) Schuttlefield, J. D.; Grassian, V. H. ATR-FTIR Spectroscopy in the Undergraduate Chemistry Laboratory. Part I: Fundamentals and Examples. *J. Chem. Educ.* **2008**, 85, 279−281.

(5) Grassian, V. H.; Schuttlefield, D. S.; Larsen, S. C. ATR-FTIR Spectroscopy in the Undergraduate Chemistry Laboratory. Part II: A Physical Chemistry Laboratory Experiment on Surface adsorption. *J. Chem. Educ.* **2008**, 85, 282−285.

(6) Feng, Z. V.; Buchman, J. T. Instrumental Analysis of Biodiesel Content in Commercial Diesel Blends: An Experimental for Undergraduate Analytical Chemistry. *J. Chem. Educ.* **2012**, 89, 1561−1565.

(7) Finlayson-Pitts, B. J.; Pitts, J. N. Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*; Academic Press: San Diego, 2000.

(8) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley & Sons, Inc.: New York, 2006.

(9) Rudich, Y.; Donahue, N. M.; Mentel, T. F. Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies. *Annu. Rev. Phys. Chem.* **2007**, 58, 321−352.

(10) Moise, T.; Rudich, Y. Reactive Uptake of Ozone by Aerosol-Associated Unsaturated Fatty Acids: Kinetics, Mechanism, and Products. *J. Phys. Chem. A* **2002**, 106, 6469−6476.

(11) Hung, H. M.; Katrib, Y.; Martin, S. T. Products and Mechanisms of the Reaction of Oleic Acid with Ozone and Nitrate Radical. *J. Phys. Chem. A* **2005**, 109, 4517−4530.

(12) Hung, H. M.; Ariya, P. Oxidation of Oleic Acid and Oleic Acid/Sodium Chloride(aq) Mixture Droplets with Ozone: Changes of Hygroscopicity and Role of Secondary Reactions. *J. Phys. Chem. A* **2007**, 111, 620−632.

(13) Thornberry, T.; Abbatt, J. P. D. Heterogeneous Reaction of Ozone with Liquid Unsaturated Fatty Acids: Detailed Kinetics and Gas-phase Product Studies. *Phys. Chem. Chem. Phys.* **2004**, 6, 84−93.

(14) Knopf, D. A.; Anthony, L. M.; Bertram, A. K. Reactive Uptake of O_3 by Multicomponent and Multiphase Mixtures Containing Oleic Acid. *J. Phys. Chem. A* **2005**, 109, 5579−5589.

(15) Hung, H. M.; Tang, C. W. Effects of Temperature and Physical State on Heterogeneous Oxidation of Oleic Acid Droplets with Ozone. *J. Phys. Chem. A* **2010**, 114 (50), 13104−13112.

(16) Zeng, G.; Holladay, S.; Langlois, D.; Zhang, Y. H.; Liu, Y. Kinetics of Heterogeneous Reaction of Ozone with Linoleic Acid and its Dependence on Temperature, Physical State, RH, and Ozone Concentration. *J. Phys. Chem. A* **2013**, 117 (9), 1963−1974.

(17) Senkan, S.; Castaldi, M.; *Combustion in Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2003.

(18) Sempere, R.; Kawamura, K. Comparative Distributions of Dicarboxylic-Acid and Related Polar Compounds in Snow Rain and Aerosols from Urban Atmosphere. *Atmos. Environ.* **1994**, 28 (3), 449−459.

(19) Worsnop, D.; Morris, J.; Shi, Q.; Davidovitsl, P.; Kolb, C. A. A Chemical Kinetic Model for Reactive Transformations of Aerosol Particles. *Geophys. Res. Lett.* **2002**, 29, 57-1−57-4.

(20) Leng, C. B.; Hiltner, J.; Pham, H.; Kelley, J.; Mach, M.; Zhang, Y. H.; Liu, Y. Kinetics Study of Heterogeneous Reaction of Ozone with Erucic Acid Using an ATR-IR Flow Reactor. *Phys. Chem. Chem. Phys.* **2014**, 16 (9), 4350−4360.

(21) Palen, E. J.; Allen, D. T.; Pandis, S. N.; Paulson, S. E.; Seinfeld, J. H.; Flagan, R. C. *Atmos. Environ., Part A* **1992**, 26, 1239−1251.

(22) Palen, E. J.; Allen, D. T.; Pandis, S. N.; Paulson, S.; Seinfeld, J. H.; Flagan, R. C. FTIR Analysis of Aerosol Formed in the Photooxidation of 1 Octene. *Atmos. Environ., Part A* **1993**, 27, 1471−1477.

(23) Molina, M. J.; Molina, L. T. Megacities and Atmospheric Pollution. *J. Air Waste Manage. Assoc.* **2004**, 54, 644−680.

(24) Fu, D.; Leng, C.; Kelley, J.; Zhang, Y. H.; Liu, Y. ATR-IR Study of Ozone Initiated Heterogeneous Oxidation of Squalene in an Indoor Environment. *Environ. Sci. Technol.* **2013**, 47 (18), 10611−10618.

(25) de Gouw, J. A.; Lovejoy, E. R. Reactive uptake of ozone by liquid organic compounds. *Geophys. Res. Lett.* **1998**, 25 (6), 931−934.