Department of Chemistry
Cumulative Examinations

December 7, 2019

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% would not yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains five examinations.

1) Analytical Cumulative Examination, Pages 1-15
2) Biochemistry Cumulative Examination, Page 16
3) Inorganic Cumulative Examination, Pages 17-23
4) Organic Cumulative Examination, Pages 24-25
5) Physical Cumulative Examination, Page 26

On your examination booklet:

1) Print your student ID number.
2) Print the Exam Booklet number.
3) Print the question number you are answering.
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**Do not write your name anywhere on the examination booklet.** Each exam will be scored anonymously. If you attempt more than one exam, you must use a separate examination booklet for each examination.

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Cume questions include the content of the manuscript itself, SI file, as well as the fundamental processes and methodologies underlying measurements employed in the study. Note that some of the measurements used in this paper were reported in greater detail in earlier publications, as indicated by the references. After careful reading of the paper and relevant literature, in your own words, answer the questions listed below. You can support your responses by making relevant notes and marks on the figures from either the manuscript itself or from the SI file. Write your Purdue ID number on the manuscript copy used in your responses and submit it along with the blue notebook.

Correct response to each of the questions below will give you 10 pts towards the cume grade.

1) Ozonolysis of α-pinene has a complex reaction mechanism leading to a large number of oxidation products. The scheme below illustrates the initial reaction steps and three major ‘first-generation’ products. Equilibrium vapor pressure of α-pinene (I) and these 3 products (II, III, and IV) are (not in any particular order): 5 Pa, 535 Pa, 7×10⁻⁵ Pa, 3×10⁻⁵ Pa. Match the values of vapor pressure to each of the molecular structures. Provide explanation for your selections.

![Diagram of ozonolysis of α-pinene](image)

2) Ozonolysis of α-pinene discussed in the paper was conducted at atmospheric pressure (101325 Pa) with the initial concentrations of α-pinene and ozone of ~200 ppb and ~500 ppb, respectively. Based on the vapor pressure values listed above, estimate which of the 3 major products will partition into the condensed phase (aerosol).
3) What are the sources of α-pinene and pyrene in the atmospheric environment? In what areas (e.g. urban, remote forests, remote marine, etc) would you expect their elevated concentrations?

4) Explain the function and/or measurement performed by each of the basic components of the Single Particle Laser Ablation Time-of-flight mass spectrometer (SPLAT) instrument shown in Figure 1.
   a) an aerodynamic lens inlet
   b) two optical detection stages with green laser
   c) pulsed infra-red (IR) laser
   d) ultra-violet (UV) excimer laser
   e) Mass detector

5) What are $d_m$ and $d_{nu}$ particle sizes and what is the relationship between them? How was the particle density of 1.18 g cm$^{-3}$ for SOA derived from the values of $d_m = 175$ nm and $d_{nu} = 207$ nm?

6) What measurement supports the assumption of the non-spherical morphology of SOA particles coated with pyrene (illustrated as A) and rules out their spherical morphology (illustrated as B). What changes in Fig 2 would you expect if pyrene coated SOA particles were spherical (illustrated as B)?

7) Mass spectrometric peaks of the individual ions measured by SPLAT appear very broad, with low $m/\Delta m$ resolution (Fig 2 panels, b, d), which is an inherent problem of single-particle laser-ablation mass spectrometry. What is the main physical reason that limits mass resolution of these instruments?

8) Write Fick’s law equation, define the variables and list their units.

9) Which equation connects the diffusivity of pyrene in SOA and viscosity of SOA? Estimate the diffusion coefficient, $D$, of pyrene in SOA if the viscosity of the latter were close to that of a liquid ($\sim 10^5$ Pa s).

10) What changes in Fig 2 (b and d) and Fig 3 would you expect if the viscosity of SOA material were comparable to that of a liquid?
Experimental determination of chemical diffusion within secondary organic aerosol particles†

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Formation, properties, transformations, and temporal evolution of secondary organic aerosol (SOA) particles depend strongly on SOA phase. Recent experimental evidence from both our group and several others indicates that, in contrast to common models' assumptions, SOA constituents do not form a low-viscosity, well-mixed solution, yielding instead a semisolid phase with high, but undetermined, viscosity. We find that when SOA particles are made in the presence of vapors of semi-volatile hydrophobic compounds, such molecules become trapped in the particles' interiors and their subsequent evaporation rates and thus their rates of diffusion through the SOA can be directly obtained. Using pyrene as the tracer molecule and SOA derived from α-pinene ozonolysis, we find that it takes ∼24 hours for half the pyrene to evaporate. Based on the observed pyrene evaporation kinetics we estimate a diffusivity of 2.5 × 10⁻²¹ m² s⁻¹ for pyrene in SOA. Similar measurements on SOA doped with fluoranthene and phenanthrene yield diffusivities comparable to that of pyrene. Assuming a Stokes-Einstein relation, an approximate viscosity of 10⁶ Pa s can be calculated for this SOA. Such a high viscosity is characteristic of tar, and is consistent with published measurements of SOA particle bounce, evaporation kinetics, and the stability of two reverse-layered morphologies. We show that a viscosity of 10⁸ Pa s implies coalescence times of minutes, consistent with the findings that SOA particles formed by coagulation are spherical on the relevant experimental timescales. Measurements on aged SOA particles doped with pyrene yield an estimated diffusivity ∼3 times smaller, indicating that hardening occurs with time, which is consistent with the increase in SOA oligomer content, decrease in water uptake, and decrease in evaporation rates previously observed with aging.

Introduction

The majority of organic aerosol, which accounts for 20–90% of the total submicron atmospheric particulate mass, consists of secondary organic aerosol (SOA). a SOA forms when volatile and semi-volatile gas-phase organic compounds are oxidized into a variety of lower vapor pressure compounds that then condense as SOA particles. A typical SOA particle comprises thousands of compounds, many of which have yet to be identified. The chemistry and physics of SOA are poorly understood and, despite significant efforts, model-predicted atmospheric SOA loadings are consistently and significantly different from field-measured loadings. a–g

Both formation mechanisms and the subsequent evolution of SOA particles are strongly affected by chemical diffusion within the SOA. High diffusivities allow SOA particles composed of semi-volatile compounds to be chemically well-mixed, achieve equilibrium partitioning between the gas and particle phases, undergo rapid heterogeneous chemistry, and evaporate, as they are transported to remote and clean environments, to maintain equilibrium with the diluted and/or reacted gas-phase. In contrast, low diffusivities impose kinetic limitations on mass transfer within the particles, causing chemical reactions with the gas-phase to be limited to the particles' surfaces, and resulting in particles that cannot maintain equilibrium with a rapidly changing gas-phase.

Until recently, SOA particles were assumed to be characterized by rapid internal mass transfer and to form well-mixed, homogeneous, "pseudo-ideal" solutions that maintain equilibrium with the gas-phase by rapid evaporation and condensation.a, A, † While it was recognized that these solutions contain a high fraction of oligomers, and might be somewhat viscous,
the prevailing belief was that diffusion in SOA is sufficiently fast to allow for mixing and equilibration on the timescale of a few minutes, which (assuming an approximate Stokes–Einstein relation) is justifiable for liquid particles with low viscosities ($10^{-3}$–$10^3$ Pa s). This assumption arose due to lack of experimental data, when little was known of the nature of SOA, but persists to this day despite clear and growing evidence to the contrary. Below, we first summarize some of the recent studies, which call for rejection of prevailing SOA models, and then introduce our current progress towards a more accurate, and thus useful, representation of SOA.

**Recent studies**

Numerous recent studies provide evidence that SOA particles contain significant amounts of high molecular weight organic compounds (oligomers), which are known to severely retard diffusion, mixing, and thus vaporization of smaller molecules, even when the oligomers are present at small concentrations. For example, Dommen et al. reported the presence of oligomers in SOA formed by photooxidation of isoprene and NOx, and found that both the relative fraction of oligomers and their molecular weight increased with time, in inverse correlation with SOA volatility. Roth et al. suggested that ambient organic particles could be in an extremely high viscosity, glassy state due to the presence of oligomeric constituents. Vaden et al. measured the room-temperature (RT) evaporation of size-selected α-pinene SOA and ambient SOA and showed that the kinetics are not those expected for well-mixed liquid droplets and are about three orders of magnitude slower than expected on the basis of prevailing SOA models. The evaporation rates reported by Vaden et al. are consistent with those reported by Grieshop et al. and Pierce et al. The former measured the evaporation of laboratory α-pinene SOA and the latter characterized the formation and evaporation kinetics of freshly formed, ultrafine ambient SOA particles and concluded that the vapor pressures of the compounds comprising SOA must be lower than $10^{-2}$ Pa, which is orders of magnitude lower than that assumed by current models. The large quantities of oligomers and extremely slow evaporation rates suggest lower than expected diffusivities (and viscosities).

In a thermal desorption study Cappa and Wilson observed that the mass spectra of evaporating α-pinene SOA particles did not exhibit the changes expected for well-mixed multi-component liquid particles and concluded that SOA must be highly viscous. Vaden et al. similarly found that the changes in particle mass spectra as a function of evaporation time are inconsistent with the assumption of high chemical diffusivities. Another recent study, of SOA formed from oxidation α-pinene by ozone and NOx radicals, reported that the measured particulate nitrate concentrations are inconsistent with equilibrium partitioning between the gas and liquid particle phases and that the data are only consistent with a highly viscous SOA.

Virtanen et al. investigated the bouncing probability of SOA particles formed from natural pine (tree) emissions and concluded that these particles are amorphous solids. Subsequent studies extended to SOA derived from several different gas-phase precursors, and again concluded that these SOA did not behave as liquids, even at relative humidity (RH) as high as 65%. Kuwata and Martin showed that the uptake of ammonia by α-pinene ozonolysis SOA particles at low RH is consistent with adsorption by a highly viscous semisolids. However, at high RH (>94% RH) SOA ammonium content increased significantly, indicating a change in SOA viscosity. Vaden et al. generated layered particles, comprising the hydrophobic liquid diocyl phthalate (DOP) and α-pinene SOA, with two opposite morphologies: SOA core coated with DOP and DOP core coated with SOA, and showed that both types of particles were stable for many hours. Given that only one of these morphologies is the thermodynamically stable form, the observed stability of both morphologies indicates that SOA must be highly viscous and diffusion in SOA must be extremely slow.

At the same time, studies by our group indicate that SOA particles cannot be rigid solids and must possess some fluidity. We showed that SOA particles generated by homogeneous nucleation followed by coagulation are spherical, providing evidence that the coagulating SOA nanoparticles could not have been rigid solids. Furthermore, we showed that coagulation during the SOA aging process results in formation of even larger, aged SOA particles, which are also spherical. In addition, SOA condensing on aspherical NaCl seed particles was shown to exhibit shape-conformity to the solid NaCl core, resulting in formation of spherical SOA-coated particles.

Despite recent and mounting experimental evidence that SOA particles are semisolids, current atmospheric models still treat them as low-viscosity solutions that equilibrate rapidly with the evolving gas phase. This assumption plays a central role in the models, and strongly influences model results both for the processes that control SOA formation and for the subsequent evolution of the system. A recent modeling study by Shrivastava et al. found large differences between volatility distributions derived from SOA growth in smog chambers and from observed SOA evaporation rates, pointing to the importance of condensed phase processes. The authors conclude that recent experimental data show that these processes result in the production of a low volatility, semisolid SOA, and point to a need to revise SOA formation, properties, and evolution in the models.

As we discuss, all experimental studies aimed to characterize the phase of SOA particles conclude that these particles are not liquid and may be characterized as “semisolids.” It is important, however, to keep in mind that the range of viscosities consistent with semisolids, and thus diffusion rates and characteristic times of mass transport and equilibration, can span over 10 orders of magnitude.

In a commissioned “perspective” article by Koop et al. the authors assess the parameters which determine whether organic particles are in semisolid states. The article, given impetus by the aforementioned recent studies, addresses the possibility of conducting direct measurements of the viscosity.
of SOA particles and concludes that such experiments present insurmountable difficulties. Here, we demonstrate that it is possible to dope SOA particles with an easily traceable compound and measure its diffusion rate through the SOA. This diffusion rate can then be used to estimate the SOA viscosity, thereby by-passing the need to accumulate large amounts of SOA or to resort to measurements on surrogate materials that do not properly represent properties of significantly more complex SOA particles.

Current work

Previously we reported evaporation rates of “pure” SOA particles produced by ozonolysis of α-pinene, and of SOA particles formed in the presence of vapors of hydrophobic organics, one of which was pyrene (a model poly-aromatic hydrocarbon, PAH). Here we report additional, more detailed, measurements of the evaporative behavior of mixed SOA-pyrene particles, as well as measurements pertaining to their sphericity or lack thereof. Data include measurements both on SOA particles formed in the presence of pyrene vapor and on SOA particles coated with pyrene subsequent to SOA formation.

The experiments are designed, first, to understand whether a typical insoluble chemical, pyrene, will reside inside the particle or on the surface, and whether the distribution of the pyrene is affected when it is introduced into the system. Second, we were interested in whether such an insoluble compound with relatively high vapor pressure (~3.5 × 10^{-4} Pa) will equilibrate with the surrounding gas-phase on the relatively rapid timescale of minutes typical of atmospheric chemistry, dilution, and local transport, or, as was found for “pure” SOA, on the much slower timescales of hours to days.

As we show below, the experiments presented here, corroborated by studies mentioned above, demonstrate that: (1) even in an environment free of organic vapor, SOA evaporation occurs on the timescale of days. (2) If an insoluble chemical (pyrene) is added after formation of SOA, it deposits on the surface of the SOA particles and evaporates rapidly when its gas-phase concentration is reduced, while the underlying SOA evaporates at the same rate as in the absence of pyrene. (3) If an insoluble chemical (pyrene) is present during formation of the SOA, it does not segregate to the surface, but is instead trapped in the interior with extremely slow diffusion/evaporation rates, while at the same time the SOA evaporation rate is reduced relative to “pure” SOA.

An analysis of the rate of evaporation of trapped pyrene is performed to obtain its estimated diffusivity through SOA (strictly, for pyrene-treated SOA); the diffusivity, 2.5 × 10^{-21} m^2 s^{-1}, is then used to estimate a SOA viscosity of 10^8 Pa s, which is consistent with the idea that SOA is an amorphous semisolid. Measurements on aged SOA particles doped with pyrene yield diffusivity ~3 times smaller, indicating that hardening occurs with time.

Finally, we repeat the diffusivity measurements using SOA doped with fluoranthene and phenanthrene, two other common PAHs, and find results comparable with those using pyrene as a tracer molecule.

Experimental

Fig. 1 presents schematics of the two experimental setups used in this study. Fig. 1a illustrates an experiment in which we studied the evaporation of SOA particles coated with pyrene subsequent to formation. “Fluoro” SOA particles were generated in the 100 L Teflon bag by the reaction of 200 ppb of α-pinene and ~500 ppb of O3 in zero air; additionally, ~250 ppm of cyclohexane was introduced into the bag as an OH scavenger. SOA size distributions were monitored using a scanning mobility particle sizer (SMPS, TSI Inc., Model 3936). Once the SOA particles stopped growing, the first differential mobility analyzer (DMA1, TSI Inc., Model 3081) was used to select an aerosol sample with a narrow distribution of mobility diameters (d_m).

These size-selected “pure” SOA particles were then passed through the coating chamber containing pyrene vapor, whose pressure is determined by controlling the temperature of a bulk pyrene sample. A thick pyrene coating was formed by creating supersaturated pyrene vapor that condensed on top of the SOA particles as they passed by. SOA particles with thin, submonolayer, pyrene coatings were generated by passing SOA particles over pyrene held at RT.

The coating process was monitored with SMPS, by measuring changes in particle d_m, while varying the temperature of the pyrene source. Once the desired coating thickness was reached, temperature was set and a second differential mobility analyzer (DMA2) was used to size-select the pyrene-coated particles. Particles were then passed through two in-line denuders and loaded into a RT evaporation chamber, partially filled with activated charcoal, where their evaporation kinetics were characterized. Particle shape, morphology, vacuum aerodynamic diameter (d_m), precise density (~0.5%), and individual particle mass spectra were periodically measured using our single particle mass spectrometer, SPLAT II. A detailed description of SPLAT II and its use for the measurement of particle properties and evaporation kinetics is provided elsewhere.

For the experiments that involved SOA formed in the presence of the vapors of pyrene, fluoranthene, or phenanthrene (Fig. 1b), a small amount of the bulk PAH was first placed at the bottom of the Teflon bag and allowed to equilibrate for ~24 hours in dry, particle-free zero air. (Note that the gas-phase PAH concentration in the Teflon bag in these experiments was equal to or lower than its saturation vapor pressure.) As before, SOA formation reaction was initiated by injecting α-pinene, O3, and cyclohexane. Once reaction was complete, SOA particles were size-selected by a DMA, transported through the denuders, and loaded into the evaporation chamber, where they were again characterized with SPLAT II as a function of evaporation time.

SOA particles formed in the presence of pyrene vapor were also aged by leaving them for ~24 hours in the Teflon bag where they were initially produced.
A detailed description of the experimental setup and methods is presented in ESI.]

Results and discussions

In an environment free of organic vapors, evaporation of "pure" α-pinene SOA reduces a particle to ∼60% of its initial mass in the first ~2 hours, after which evaporation significantly slows, such that ~30% of the particle mass still remains following 24 hours of evaporation. SOA particles aged for ~24 hours before they are placed in the evaporation chamber evaporate even more slowly. As shown in Fig. 1, pyrene, a prototypical PAH, can either be added after formation of SOA particles or be present during SOA generation. These two schemes (which serve to model two different environmental conditions) yield quite different types of particles and quite different subsequent physiologies. When added to pre-existing SOA particles, pyrene is seen to reside at the surface of the SOA as solid nodules. Before the addition of pyrene, SOA seed particles size-selected at $d_m = 175$ nm have a $d_{ev}$ distribution (shaded, green curve in Fig. 2a) with a narrow line-width (full width at half maximum, FWHM, of 6.5%) indicative of spherical particles. The peak position of the $d_{ev}$ distribution ($d_{ev} = 207$ nm) together with the particle mobility diameter yields the density 1.18 g cm$^{-3}$ for "pure" SOA, in agreement with our previous measurements. Exposure to supersaturated pyrene vapor both enlarges the particles and causes broadening of the size distribution. In Fig. 2a we show the observed temporal evolution of the measured $d_{ev}$ distribution of pyrene-coated particles which were first size-selected by DMA2 at $d_m = 400$ nm and then loaded into the evaporation chamber. A significant increase in the initial ($t = 0$, blue trace in Fig. 2a) $d_{ev}$ line-width (FWHM of 28%) indicates that the pyrene-coated SOA particles are spherical and that the condensed pyrene has formed nodules on top of the spherical SOA core.

Evaporation of these pyrene-coated SOA particles in an environment free of organic vapor results in rapid (~1 hour) loss of the pyrene and re-emergence of the initial spherical particle shape, but with smaller diameter. In Fig. 2b, the mass-spectral data from sampled particles show rapid evaporation of pyrene, easily identifiable by its parent ion peak at $m/z = 202$, on the same timescale as the changes in particle shape in Fig. 2a. Fig. 3 shows the relative fraction of particle-bound pyrene as a function of evaporation time, derived from integration of the intensities of pyrene characteristic mass-spectral peaks. The data for thick pyrene coating (green symbols) show a rapid decrease in the pyrene intensity as it rapidly evaporates. Based on the measured particle $d_m$ and $d_{ev}$ before and after coating, and the densities of pure SOA and pyrene we calculate a dynamic shape factor of 1.32, pyrene volume equivalent diameter $d_{v_{PAH}}$ of 304 nm, and pyrene weight fraction of 85% for these pyrene-coated particles. Following rapid pyrene evaporation, the particles become again spherical and have mass spectra representative of "pure" SOA with no residual pyrene present. Given that the instrument is extremely sensitive to pyrene (it can easily detect sub-monolayer quantities), we can confidently conclude that these data rule out the possibility of any significant diffusion of condensed pyrene into the SOA core.
The rate of SOA loss during this process is similar to that which takes place in “pure” SOA, indicating that nodules of pyrene cover only a fraction of the SOA surface and that the SOA was not modified in response to the pyrene that was on the surface. When SOA particles are exposed to pyrene at its saturation vapor pressure, they acquire a thin coating of pyrene, the thickness of which was determined from an observed 2 nm increase in $d_{va}$ of the coated particles, as measured by SPLAT II. Taking particle density into account this change in $d_{va}$ yields a coating thickness of 0.8 nm. These coated particles remain spherical according to our measurements and evaporate at a rate that is virtually indistinguishable from “pure” SOA particles, while the thin pyrene layer evaporates so quickly that after 60 minutes no pyrene is detectable in these particles (Fig. 3, blue symbols).

In contrast to the surface pyrene coatings, significantly different behavior occurs when pyrene vapor, at or below its saturation vapor pressure, is present during formation of SOA (Fig. 1b). In this case, pyrene becomes incorporated directly into the particles’ interiors and remains trapped there. These pyrene-containing SOA particles form as spheres and remain spherical during evaporation, as evident from the narrow line-widths of their $d_{va}$ distributions shown in Fig. 2c. The evaporation of both the SOA and pyrene is now extremely slow.

Fig. 2 Temporal evolution of the vacuum aerodynamic diameter distribution of pyrene-coated SOA particles (a) and SOA particles formed in the presence of pyrene vapor (c); corresponding changes in the particle mass spectra with evaporation time for pyrene-coated pure SOA particles (b) and SOA particles formed in the presence of pyrene vapor (d). The parent ion peak of pyrene is at m/z = 202.

Fig. 3 Fraction of pyrene mass-spectral intensity as a function of evaporation time, for pyrene-coated SOA particles (green and blue), fresh SOA particles with trapped pyrene (red), and aged SOA particles with trapped pyrene (brown). For each of the two “coating” data sets, the pyrene content of the last point was below detection limits. Lines drawn for coated particles are guides to the eye, while lines through the data for internal pyrene are fits to eqn (2). For all cases the data point at $t = 0$ is normalized to 1.

The temporal evolution of the $d_{va}$ distribution and mass spectra of size-selected ($d_{nm} = 175$ nm) SOA particles formed in the presence of pyrene vapor are shown in Fig. 2c and 2d, respectively. After ~24 hours of evaporation SOA particles formed in the presence of pyrene vapor lose only ~20% of their volume or
~7% of their initial diameter\textsuperscript{14,26} and still contain a large fraction of their initial pyrene content (Fig. 2d).

Fig. 3 shows, as a function of evaporation time, the relative fraction of pyrene remaining in SOA particles formed in the presence of pyrene vapors (red symbols). There is a stark difference between particles with pyrene added after SOA formation and those with pyrene incorporated during SOA formation. While pyrene added to the particle surface (after particle formation is complete) is deposited on the SOA surface and evaporates quickly, particles formed \textit{in the presence} of pyrene vapor still contain \textasciitilde50% of the initial amount of pyrene even after \textasciitilde24 hours of evaporation. Based on the pyrene evaporation data presented in Fig. 3 it is possible to calculate and compare the pyrene loss rates from two particles types. In the case of the particles with pyrene surface coating, \textasciitilde95% of the particle initial pyrene content ($c_{0}^\text{PMH} = 304 \text{ nm and density = 1.27 g cm}^{-3}$) is lost in \textasciitilde100 min, yielding a pyrene loss rate of $5.3 \times 10^{5} \text{ molecules min}^{-1} \text{ particle}^{-1}$. In contrast, SOA particles formed in the presence of pyrene vapor lose half of their initial pyrene content (~5% of the SOA particle mass\textsuperscript{26}) in 1400 min, yielding a pyrene loss rate of 190 molecules min\textsuperscript{-1} particle\textsuperscript{-1}, which is ~3000 times slower than the loss rate of the pyrene surface coating.

This simple comparison clearly indicates that when pyrene is present during production of SOA, it becomes incorporated into the interior of the particle, from which it can escape on timescales that are determined by pyrene diffusion through viscous SOA.

In addition, we find that particle aging further decreases the slow rates of SOA evaporation and internal pyrene loss; this mirrors the effect of aging on the evaporation of “pure” SOA and also SOA formed in the presence of different hydrophobic organic vapors.\textsuperscript{14,26} It can be seen in Fig. 3 that after \textasciitilde24 hours of evaporation these aged particles still contain \textasciitilde70% of the initial amount of pyrene acquired during SOA formation. Clearly, chemical and/or physical transformations in SOA (e.g., oligomerization) continue long after particle formation, and the aging of SOA further reduces the diffusion rate of pyrene incorporated into the bulk of a particle.

The chemical and physical nature of SOA particles, and why the equilibration kinetics are so slow, are still matters of conjecture. However, directly inferable from these experimental results and other recent studies\textsuperscript{14,18,21,23,26} are the facts that SOA does not form well-mixed, homogeneous solutions that maintain rapid equilibrium with the gas-phase. When gas-phase organic concentrations decrease, the evaporation of pure SOA particles is so slow that they might equilibrate with the surrounding gas only on the timescale of days. Even organic compounds with higher volatilities can get trapped within the highly viscous SOA phase, and experience severe diffusion limitations on their evaporation from these particles.\textsuperscript{14,18,19,26}

In contrast, insoluble volatiles introduced after particle formation reside only on the surface and evaporate rapidly when their gas-phase concentrations are reduced.

In two recent papers that discuss the relevance of SOA diffusion coefficients, viscosity, and equilibration time on atmospheric processes the authors note that at present it is not known whether SOA particles are low viscosity liquids, amorphous or glassy solids, or semisolids.\textsuperscript{25,26} Even the viscosities of what have been called “semisolids” span many orders of magnitude: from $\sim 10^{4}$ to $10^{12} \text{ Pa s}$. A reasonable estimate of diffusion rates through SOA, and thus its viscosity, can now be obtained from the measurements presented in Fig. 3.

As a first approximation, we assume Fickian diffusion. We consider the loss of pyrene incorporated in fresh SOA formed in the presence of pyrene vapor, making the simplifying approximation that particle size and diffusivity remain constant over the experiment. For a sphere with boundary conditions of uniform pyrene concentration $C_{0}$ at $t = 0$, and $C = 0$ at the particle’s surface, solution (of Fick’s Law) for time-dependent concentration is given as\textsuperscript{31}

$$C(r, t) = \frac{2R_{0}C_{0}}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin(\lambda r) e^{-D_{l} \lambda^{2} t} \quad (1)$$

where $\lambda = m/2n$. Here, $R_{0}$ is the radius of the sphere, which in this case is ~87.5 nm, and $D_{l}$ is the diffusivity of the pyrene. Integration over the volume of the sphere gives the total fraction of pyrene remaining at any time as:

$$\left[6/(\pi R_{0}^{3})\right] \sum_{n=1}^{\infty} \frac{(-1)^{n}}{n} R_{0} \cos(\lambda R_{0})/\lambda - \sin(\lambda R_{0})/\lambda^{2} e^{-D_{l} \lambda^{2} t} \quad (2)$$

A fit of the long-term pyrene evaporation data to eqn (2) (Fig. 3) yields $D = 2.5 \times 10^{-21} \text{ m}^{2} \text{ s}^{-1}$. The initial sharp drop in pyrene concentration is attributed to rapid evaporation of a sub-monolayer of pyrene residing on the particle surface, consistent with the fast evaporation observed for thin pyrene coating (Fig. 3, blue symbols).

Fig. 4 displays the calculated temporal evolution in pyrene concentrations relative to $t = 0$ as a function of the distance from the particle center, showing that pyrene is lost mostly from near the particle surface and that even after ~24 hours of evaporation,
the pyrene concentration at the particle center remains unchanged.

Viscosity, $\eta$, can be estimated through the Stokes–Einstein equation:

$$\eta = kT/4\pi a D$$  \hspace{1cm} (3)

where the “slip” boundary conditions have been used and $a$ is the hydrodynamic radius of a molecule of pyrene. An estimate of $a = 0.4 \text{ nm}$ yields a SOA viscosity of $3 \times 10^{\text{a}} \text{ Pa s}$. However, a study of the diffusivity of pyrene in water yields a hydrodynamic diameter for pyrene of 1.1 nm,\textsuperscript{23} indicating that the diffusing species are most likely pyrene clusters consisting of $\sim 30$ molecules. This is consistent with our findings that pyrene forms nodule-like clusters when coating hydrophilic seed particles.\textsuperscript{24,29} If pyrene within SOA particles is present not as individual molecules, but rather in the form of small clusters, these clusters would have a slightly greater value of $a$, and thus the estimate of $\eta$ would be slightly lower. For example, clusters that contain as many as $\sim 1000$ pyrene molecules ($a = 4$ nm) will yield a SOA viscosity of $3 \times 10^{\text{a}} \text{ Pa s}$. Note that if the entire initial pyrene content of an SOA particle ($\sim 5\%$ of the SOA particle mass) was to form a single crystal, it would result in $a = 29$ nm. However, the significant effect that incorporated pyrene has on the SOA evaporation rate, the steady loss of pyrene as a function of time, and highly reproducible individual particle mass spectra indicate that it must be dispersed throughout the entire particle and diffuse out as relatively small clusters, thus the value calculated for $\eta$ will not differ much from $3 \times 10^{\text{a}} \text{ Pa s}$.

Fig. 3 (brown symbols) shows that pyrene evaporation from aged ($\sim 24$ hours) SOA particles is even slower, indicating that the SOA viscosity increases with time. The fit to these data, under the above assumptions, $R_s = 120 \text{ nm}$, and with $a = 0.4 \text{ nm}$, yields $D = 1 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$, and a SOA viscosity of $8 \times 10^{\text{a}} \text{ Pa s}$.

A viscosity of $\sim 10^{\text{a}} \text{ Pa s}$, for fresh SOA, is equivalent to that of tan,\textsuperscript{25,30,24,35} and the substance would normally be considered to be semisolubil. Again, this is entirely consistent with the recent experiments by several research groups,\textsuperscript{14,18-21,21,26} who, based on entirely different types of experiments, conclude that SOA is an amorphous solid or semisolubil.

In Fig. 5 we show the results for $\pi$-pinene SOA formed in the presence of two other PAHs: phenanthrene, with a molecular weight of 178 and a vapor pressure of $1.6 \times 10^{\text{a}} \text{ Pa}$, and fluoranthene, with a molecular weight of 202 and a vapor pressure of $1.2 \times 10^{\text{a}} \text{ Pa}$. The solid lines in the figure represent best fits to the PAH long-term evaporation data, yielding diffusivities of $1.5 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$, similar to pyrene. As in the case of pyrene, the initial sharp drop in sub-monolayer of PAHs concentrations is attributed to rapid evaporation of a sub-monolayer of PAHs remaining on the particle surface.

While SOA particles are viscous enough to prevent rapid diffusion, and even to bounce as solid particles, they have sufficient fluidity to coalesce into spheres within minutes.\textsuperscript{23,24} It is therefore reasonable to ask whether this observation is consistent with such a large viscosity as estimated above.

The timescale for coalescence of two adjoined spheres driven by surface tension, $\sigma$, can be estimated\textsuperscript{26} as:

$$\tau = \eta R_s^2 / \sigma$$  \hspace{1cm} (4)

Surface tensions (in air) of the small organic acids, esters and ketones, of which SOAs are at least partially composed, are typically $\sim 20 \times 10^{-3} \text{ J m}^{-2}$. Assuming, again, $R_s = 87.5 \text{ nm}$ and a viscosity of $\sim 10^{\text{a}} \text{ Pa s}$ this gives a timescale $\tau = 7 \text{ minutes}$ for forming a sphere, which is less than the time required to prepare and then characterize the particles. For smaller particles present during SOA nucleation and growth, this timescale is reduced to seconds.

While these calculations are based on some approximations, and Fickian diffusion with Stokes–Einstein scaling is not the only possibility, the above formulation has the distinct advantage of being consistent with several experimental observations and the result is expected to provide a more accurate picture of the kinetics of chemical equilibration in SOA than hitherto available.

Conclusions

The experiments presented here, and corroborated by other recent studies already reported by this and other groups,\textsuperscript{14,17,10,20,26} demonstrate that: (1) in a room-temperature environment free of organic vapor, rather than undergoing rapid equilibration with the gas phase, SOA evaporates at first on the relatively slow time-scale of hours followed by the extremely slow time-scale of days. (2) If molecules such as pyrene (a hydrophobic organic) are introduced subsequent to SOA formation, they will deposit on the particle surface, will not diffuse into the particle bulk, and will evaporate rapidly when their gas-phase concentration is reduced. (3) If molecules, such as pyrene, are present during SOA formation, they become trapped in the interior and exhibit...
extremely slow diffusion and therefore slow evaporation rates, while at the same time the SOA evaporation rate is reduced relative to "pure" SOA. (4) The evaporation kinetics of trapped molecules, like pyrene, is directly related to their diffusion in SOA. (5) The observed evaporation rate of trapped pyrene from fresh α-pinene SOA yields an estimated diffusivity of $2.5 \times 10^{-21}$ m$^2$ s$^{-1}$ (and $1.5 \times 10^{-21}$ m$^2$ s$^{-1}$ for fluoranthene and phenanthrene). (6) Diffusivity decreases by a factor of ~3 when the SOA is allowed to age for ~24 hours. (7) The measured diffusivity can be used to estimate a viscosity of ~10$^8$ Pa s for SOA, which is consistent both with the observation that the particles are rigid enough to bounce as solids and the fact that they are sufficiently fluid for surface tension to produce spheres on a time scale of minutes.

All evidence indicates that chemical diffusion through SOA is many orders of magnitude slower than is consistent with the assumptions of prevailing atmospheric models, which require a well-mixed solution, and that these particles cannot maintain reversible equilibrium with the more rapidly changing gas-phase.

Finally, it is necessary to consider how the wide range of temperatures, RHs, and types of SOA occurring in the atmosphere might affect the above conclusions. A recent study on the bounce of SOA particles at RH below 65% suggests that some SOA softens slightly with increased RH. It is thus probable that under average atmospheric conditions viscosities in these particles will still be extremely high. Based on the hygroscopic growth factors of SOA, we expect uptake of water, and thus changes in particle viscosity and diffusivities, to be significant only at RH above ~95%, consistent with recent observations of increased ammonia uptake by SOA at RH > 94%. Still, to satisfactorily generalize these findings to the behavior of SOA particles in the atmosphere, there is a clear need to extend these measurements to SOA produced from a broader range of precursors, investigate the effect of inorganic seeds on the same, and conduct the experiments over a range of relative humidity and temperature.

Acknowledgements

This work was supported by the U. S. Department of Energy Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Bioscience Division and Office of Biological and Environmental Research (Atmospheric Research Program). This research was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research at Pacific Northwest National Laboratory (PNNL). PNNL is operated by the US Department of Energy by Battelle Memorial Institute under contract No. DE-AC06-76RL01830.

References

SUPPORTING INFORMATION

Experimental Determination of Chemical Diffusion within Secondary Organic Aerosol Particles

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TITLE RUNNING HEAD: SOA: viscosity and diffusivity

Experimental Setup

Figures 1a and 1b provide a schematic of the experimental setup used to generate pyrene-coated pure SOA particles and SOA particles formed in the presence of PAHs vapors, respectively.

In experiments with pyrene-coated pure SOA particles, pure SOA particles are generated in a smog chamber by injecting 200 ppb of α-pinene, ~500 ppb of O₃, and ~250 ppm of cyclohexane, used as an OH scavenger, into a 100 L Teflon bag. Particle size distributions are periodically monitored using a scanning mobility particle sizer (SMPS, TSI Inc., Model 3936). All SMPSs and differential mobility analyzers (DMAs) used to select aerosol samples with narrow distributions of mobility diameters (dₘ) are calibrated using NIST-certified size standards, spherical polystyrene latex (PSL) beads of known diameters. Once SOA particles stop growing, they are classified with the first DMA (DMA1, TSI Inc., Model 3081) and the mono-disperse particles are passed through a coating chamber containing pyrene vapor, whose vapor pressure is controlled by varying the pyrene source temperature. When SOA is passed over the pyrene source held at room temperature (RT), the SOA particles acquire a sub-nanometer thick pyrene coating, producing SOA particles that contain slightly less than ~2% pyrene by weight.

This coating thickness is determined by measuring the vacuum aerodynamic diameter (dₐₒ) of the DMA-classified particles before and after coating process. Using measured changes in dₐₒ and the SOA density, determined from measured dₐₒ and dₘ, we calculate thickness of 0.8±0.3 nm for the thin pyrene coating.
To generate SOA with a thicker pyrene coating, the pyrene source is heated to generate supersaturated pyrene vapor that condenses on the SOA seed particles as they pass through it. The coating process is monitored with DMA2 and the coating “thickness” is controlled by varying the source temperature. The coated particles are classified with DMA2 to select monodisperse particles with uniform SOA core and uniform coating thickness.

Coated SOA particles are passed through the two inline denuders filled with activated charcoal, and loaded into the evaporation chamber that is partially filled with activated charcoal and kept at RT. Particle shape, morphology, \( d_{\text{w}} \), precise density, and composition through individual particle mass spectra are periodically measured with our single particle mass spectrometer, SPLAT II.\(^{1,6}\) Typical evaporation experiments take ~24 hours.\(^1\) The evaporation of SOA particles coated with a sub-nanometer of pyrene was monitored for 2 hours, until pyrene had evaporated to below detection.

A detailed description of SPLAT II, its characteristic measurement capabilities, and a complete account of RT evaporation kinetics experiments are provided elsewhere.\(^{1,6}\) Here we provide only a very brief description.

SPLAT II uses an aerodynamic lens inlet to efficiently transport particles into the vacuum and generate a collimated particle beam, in which particle velocity is related to particle vacuum aerodynamic diameter, \( d_{w} \). Each particle is detected in two optical detection stages and the measured particle time-of-flight between the two stages is used to calculate particle velocity, yielding particle \( d_{\text{w}} \). The relationship between particle velocity and \( d_{\text{w}} \) is calibrated using NIST-certified PSL particles. SPLAT II has sizing precision that is better than 0.5%,\(^7\) making it possible to measure the density of particles classified by a DMA with precision of ±0.5%\(^5\).

The two optical detection events are also used to generate triggers to the pulsed infra-red (IR) and ultra-violet (UV) excimer lasers. The IR laser (GAM Lasers, Model EX5/200, 9.4 μm) is used to evaporate the volatile fraction of each particle and the time-delayed UV laser (GAM Lasers, Model EX5/300, 193 nm) is used to ionize the molecules in the expanding plume of evaporating gas. The ions are detected and analyzed with an angular reflecton time-of-flight mass spectrometer (TOF-MS, R. M. Jordan Inc., Model D-850). The two-step ion generation scheme, provides significant improvement on the instrument quantitative capabilities.\(^6\)

Moreover, in SPLAT II the line-shape and position of the \( d_{w} \) distribution of mono-disperse particles can be used to determine particle shape and high precision density, with spherical particles having narrow line-shape and aspherical particles exhibiting broad \( d_{w} \) size distributions.\(^3\) Particle morphology is characterized by utilizing a depth-profiling approach.\(^5\)

Figure 2a shows that the \( d_{w} \) distribution of pure SOA core particles classified with DMA1 at \( d_{w}=175 \) nm (green shaded peak) peaks at 207 nm and has a narrow line-width (full width at half maximum, FWHM, of 6.5%), consistent with spherical particles whose density is 1.18 g/cm\(^3\), in agreement with our previous measurements.\(^3\) The \( d_{w} \) distribution of pyrene-coated SOA particles classified at \( d_{w}=400 \) nm peaks at 308 nm and has FWHM of 28%, providing unequivocal evidence of particle asphericity and large dynamic shape factor. As pyrene coating evaporates, the line-width of the \( d_{w} \) distribution decreases, indicating a transformation of aspherical pyrene-coated particles into spherical pure SOA particles, consistent with the mass spectra.

It is possible to use the known SOA and pyrene densities, the size of the SOA core, and the measured \( d_{w} \) and \( d_{\text{w}} \) for pyrene-coated particles to calculate the pyrene volume fraction and the average particle dynamic shape factor following the equations below.
\[ m_p = \frac{\pi}{6} (d_{w})^3 \rho_p \]  

(S1)

Where \( m_p \) is particle’s mass, \( d_{w} \) is particle’s volume equivalent diameter, and \( \rho_p \) is particle’s density.

\[ d_n = d_w \chi_t \frac{C_t(d_w)}{C_e(d_w)} \]  

(S2)

Where, \( d_n \) is particle’s mobility diameter, \( \chi_t \) is the dynamic shape factor (DSF) in the transition regime, and \( C_t(d_n) \) and \( C_e(d_n) \) are the Cunningham slip correction factors.

\[ d_a = \frac{\rho_0 d_w}{\rho_0 \chi_n} \]  

(S3)

Where \( d_a \) is particle’s vacuum aerodynamic diameter and \( \chi_n \) is the particle DSF in the free-molecular regime.

For spherical particles \( \chi_t = \chi_n = 1 \), \( d_s = d_a \), and \( d_w = \frac{\rho_0 d_a}{\rho_s} \) \( d_w = d_a \) \( \rho_0 \).

When particle \( d_w \) is unknown, Equations S1-S3 can be used to calculate an average DSF under the approximation that \( \chi_t = \chi_n = \bar{\chi} \) according to:

\[ d_w = \frac{\rho_0}{\rho_s} \frac{1}{\chi_n \chi_t} \frac{C_t(d_w)}{C_e(d_w)} \frac{\rho_0 \chi_n}{\chi_t} \frac{1}{\rho_s} \frac{C_s(d_w)}{C_t(d_w)} \]  

(S4)

Using volume and mass additivity, for pyrene-coated particles

\[ m_p = \frac{\pi}{6} \left[ \rho_{SOA}(d_{w}^{SOA})^3 + \rho_{PM}(d_{w}^{PM})^3 \right] \]  

(S5)

\[ (d_w)^3 = (d_w^{SOA})^3 + (d_w^{PM})^3 \]  

(S6)

Where, \( d_{w}^{SOA} \) is the volume equivalent diameter of the SOA seed of the pyrene-coated particle, \( d_{w}^{PM} \) is volume equivalent diameter of pyrene of these particles, \( \rho_{SOA} \) is SOA density, and \( \rho_{PM} \) is pyrene density.

For pyrene-coated particles with \( d_w = 400 \) nm, \( d_w = 308 \) nm, \( d_{w}^{SOA} = 175 \) nm, \( \rho_{SOA} = 1.18 \) g cm\(^{-3}\), and \( \rho_{PM} = 1.27 \) g cm\(^{-3}\). Equations S1 to S6 yield an average DSF of \( \bar{\chi}_{\text{av}} = 1.32 \), pyrene volume fraction of 84%, and pyrene weight fraction of 85%.

SOA particles formed in the presence of PAHs vapors are generated under conditions identical to those for pure SOA particles, except that prior to the experiment small amount of bulk PAH sample is loaded into the smog chamber filled with particulate-free zero-air and left for ~24 hours to equilibrate. Once SOA formation is complete, particles are classified, passed through the desanders into the evaporation chamber and characterized as function of evaporation time as described above.

Aged SOA particles are generated by leaving the particles in the smog chamber for ~24 hours before they are studied.

To determine the particles’ pyrene content, mono-disperse samples of pure pyrene, pure SOA particles, and pyrene-containing SOA particles with known diameters and loadings were characterized by the Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.). \(^{14, 15}\) which was used to quantify the relative and absolute intensities of non-overlapping peaks characteristic of pyrene and SOA. Based on the mass-spectral calibrations of pure SOA and pure pyrene particles the relative content of pyrene trapped in SOA particles was determined to be ~5%.
REFERENCES


Biochemistry Cumulative Exam

Nucleic Acids

December 7, 2019

1. Most gene promoters and origins of replication are rich in adenine and thymidine.

   a) Provide a biochemical reason why this base composition is advantageous. (10 points)

   b) Draw an A-T base pair. The bases must be in their nucleotide form, and the hydrogen bond(s) clearly shown for full credit. (15 points)

2. DNA replication is a semi-conservative process. Explain what that means. (5 points)

3. The number of eukaryotic genes is far smaller than the number of mRNAs and proteins that have been identified. Provide an explanation for how this is possible. (10 points)

The following questions are based on the article “RNA-dependent RNA targeting by CRISPR-Cas9”. Strutt, S.C. et al eLife 7 (2018).

5. a) Explain the roles of CRISPR and Cas in the prokaryotic “immune system”. (10 points)

   b) How do prokaryotes "remember" previous infections? (10 points)

6. Describe HOW the Cas9 enzymes were tested for their ability to cleave RNA. Your answer must explain what type of experiment was used, how the reactions were assessed for nucleic acid cleavage, and how the data is interpreted. Copying the methods section will not answer this question.

7. Cas9 enzymes cleave dsDNA and ssDNA more efficiently than they cleave ssRNA. Provide a structural and biochemical explanation for this observation. (10 points)

8. Give an example of when it may be advantageous to regulate gene expression through CRISPR-Cas editing of RNA, rather than editing the DNA in a cell or organism. (10 points)
Cume Exam – Inorganic Division

December 7, 2019

Topic: Migratory Insertion

1. (10 points) Migratory insertion is a fundamental organometallic reaction, where an anionic and neutral ligand on a metal couple to generate a new ligand. Draw a general example of this reaction, using M for the metal, X for the anionic ligand, and YZ for the neutral ligand.

2. (10 points) Give 2 general features of the migratory insertion reaction.

3. (10 points) Migratory insertion reactions are classified by the way the neutral ligand inserts into the anionic ligand. Both 1,1- and 1,2-insertions have been observed as reported in the literature. Explain the difference between these two insertion types. Feel free to use an example of each to help make your explanations more clear.

4. (35 points) Read the attached communication entitled “Synthesis, Structure, and Reactivity of an NHC Silyl Gold(I) Complex” by Maximilian Joost, Nathalie Saffon-Merceron, Abderrahmane Amgoune, and Didier Bourissou* that was recently published in the ACS journal, Organometallics (Organometallics 2019, 38,3494). In this manuscript, the authors report the synthesis of a gold-silyl species that does migratory insertion of a functionalized acetylene.

   a. What is the oxidation state, d electron count, and valence electron count of Au in compound 1?

   b. In the crystal structure of 1, the authors mention a trans influence with respect to the NHC and silyl ligands. What is that referring to?

   c. Explain the significance of migratory insertion into a gold-silyl bond.

   d. What is the oxidation state, d electron count, and valence electron count of Au in compound 2? What does this tell you about the migratory insertion process?

   e. Migratory insertion of methyl propiolate was initially confirmed using high resolution mass spectrometry. Why is this technique not definitive characterization? What combination of methods were the authors able to use to definitively show that insertion had indeed occurred?

   f. Please draw a complete mechanism for the migratory insertion reaction discussed in this paper. Make sure to include a proposed a transition state for how you think this happens.

   g. Explain the regioselective preference for how this insertion occurs.
5. (25 points) Provide the products for the following migratory insertion reactions:
6. Please show the mechanisms for the reactions below. For full credit, show every step.

a. (10 points)

\[
\begin{align*}
\text{Zr} & \quad \text{Cl} \\
\text{H} & \quad \text{ethylene} \\
\text{Zr} & \quad \text{Cl} \\
\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

b. (challenge: 10 points bonus – you must get the whole mechanism for credit)

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Co} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{Ph}_3\text{P} & \quad \text{Co} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{C}_2\text{H}_4 & \quad \text{ethylene} \\
\text{CH}_4 & \quad \text{methane}
\end{align*}
\]
Synthesis, Structure, and Reactivity of an NHC Silyl Gold(I) Complex

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Supporting Information

ABSTRACT: The first example of a silyl gold(I) complex stabilized by an N-heterocyclic carbene (NHC) was synthesized and fully characterized, including crystallographically. The syn insertion of methyl propiolate into the Au–Si bond leading to a vinyl gold complex is reported. As substantiated by X-ray diffraction analysis, the reaction proceeds with opposite regioselectivity compared with that previously observed with phosphine silyl gold(I) complexes.

During the last 15 years, homogeneous gold catalysis has rapidly evolved and now occupies a prominent position in organic chemistry.¹⁻⁴ The activity of gold catalysts is largely based on the π-acidic property of cationic gold complexes, allowing for the activation of CC multiple bonds toward nucleophilic attack.⁵ Whereas this activation mode is nowadays well understood and broadly used, other reaction patterns commonly encountered in transition-metal catalysis, for example, oxidative addition, reductive elimination, or migratory insertion, are much less explored.

In the context of an ongoing research program in our group devoted to the investigation of unusual elementary steps of gold,⁶ we reported in 2013 reactions of phosphine silyl gold(I) complexes with alkynes and allenes. This work provided unambiguous evidence of syn insertion reactions at gold (Scheme 1A),⁷,⁸ a process in sharp contrast with the outer-sphere anti addition pathway usually encountered in gold catalysis.⁹,¹⁰ A comprehensive mechanistic study revealed that a two-step coordination-insertion mechanism is operating.¹⁰ Migratory insertions of alkynes into Au(III)–C bonds were then authenticated.¹¹⁻¹⁷

As a further extension of this work, we have now investigated analogous silyl gold(I) featuring N-heterocyclic carbene (NHCs) instead of phosphines (Scheme 1B). NHCs play a major role in gold catalysis¹⁸ and have been shown to stabilize a large set of reactive gold(I) compounds, including species not accessible to other ancillary ligands. Most noteworthy are the gold(I) fluoride and hydride complexes reported by Nolan, Sadighi, and Toste.¹⁹⁻²³ Unlike silyl copper(I) complexes, which are well known and commonly involved in catalytic transformations,²⁴⁻²⁶ analogous silyl gold(I) species remain scarce. NHC boryl gold(I) complexes have been reported,²⁷,²⁸ but to the best of our knowledge, NHC silyl gold(I) complexes are hitherto unknown. Here we report the synthesis and characterization of such a compound, namely, [(IPr)Au(SiMe₃Ph)] (I) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). It is shown to react with methyl propiolate via syn insertion of the alkyne with opposite regioselectivity compared with that observed with phosphine silyl gold(I) complexes.

Scheme 1. Reaction of Methyl Propiolate with Phosphine versus NHC Silyl Gold(I) Complexes

As a further extension of this work, we have now investigated analogous silyl gold(I) featuring N-heterocyclic carbene (NHCs) instead of phosphines (Scheme 1B). NHCs play a major role in gold catalysis¹⁸ and have been shown to stabilize a large set of reactive gold(I) compounds, including species not accessible to other ancillary ligands. Most noteworthy are the gold(I) fluoride and hydride complexes reported by Nolan, Sadighi, and Toste.¹⁹⁻²³ Unlike silyl copper(I) complexes, which are well known and commonly involved in catalytic transformations,²⁴⁻²⁶ analogous silyl gold(I) species remain scarce. NHC boryl gold(I) complexes have been reported,²⁷,²⁸ but to the best of our knowledge, NHC silyl gold(I) complexes are hitherto unknown. Here we report the synthesis and characterization of such a compound, namely, [(IPr)Au(SiMe₃Ph)] (I) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). It is shown to react with methyl propiolate via syn insertion of the alkyne with opposite regioselectivity compared with that observed with phosphine silyl gold(I) complexes.

By analogy to the synthesis of phosphine silyl gold(I) complexes,²⁹,³⁰ we envisioned preparing an NHC silyl gold(I) complex via salt metathesis between an NHC gold(I) chloride precursor and a lithiosilane. The commercially available complex [(IPr)AuCl] (IPr = 1,3-bis(2,6-diisopropylphenyl)-phenylimidazol-2-ylidene) was chosen as the precursor. Phosphine silyl gold(I) complexes require important steric protection at silicon to be isolated, typically SiPh₃, Si(bu)₃Ph, or Si(SiMe₃)₃.³¹,³²,³³ We surmised that the strong σ-donor character and high steric demand of IPr might enable the synthesis of an NHC silyl gold(I) complex featuring relatively small substituents at silicon. Starting from chlorodimethylphenylsilane and lithium metal, the corresponding lithiosilane was prepared and in situ reacted with [(IPr)AuCl] (Scheme 2).

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Scheme 2. Synthesis of Complex 1

\[
\begin{align*}
\text{PhMe}_2\text{Si} \text{Cl} & \quad \xrightarrow{1/2 \text{Li THF, RT overnight}} \quad \text{Dipp} \text{Au-SiMe}_2\text{Ph} \\
2/4(\text{IPr} \text{AuCl}) \text{THF, 0 }^\circ\text{C} \quad & \text{2 min} \quad \xrightarrow{1 \text{ (75%)}} \quad \text{Au-SiMe}_2\text{Ph}
\end{align*}
\]

\text{"Dipp = (2,6-diisopropyl)phenyl."

The ensuing complex 1 was thereby obtained as a white solid in 75% isolated yield. It was characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry (HRMS).

The following data are diagnostic for a silyl gold complex. The \text{^{29}Si} NMR spectrum of 1 exhibits a singlet resonance at \(\delta\) 12.9, in the same range as those previously reported for phosphine silyl gold(1) complexes.\textsuperscript{\text{2,10}} In the \text{^{13}C} NMR spectrum, a singlet resonance at \(\delta\) 217.4 is observed for the carbene carbon, significantly shifted downfield compared with that of \([\text{IPr} \text{AuCl}]\) \(\delta = 175.1\text{.}\textsuperscript{\text{3,11}}\) The downfield shift of the carbene carbon signal results from the strong trans influence of the silyl group\textsuperscript{\text{3,12}} and is comparable to that reported by Sadighi for the hydride complex \([\text{IPr} \text{AuH}]\) \(\delta = 204.9\text{.}\textsuperscript{\text{23}}\)

The molecular structure of 1 was further analyzed by X-ray diffraction (Figure 1). Accordingly, complex 1 was found to adopt a discrete monomeric structure in the solid state without a Au--Au intermolecular interaction. (The shortest Au--Au distance exceeds 8 Å.) The gold atom is two-coordinate and quasi linearly bonded to the NHCS and silyl ligands (\text{CAuSi} 171.6(1)\textsuperscript{\text{9,5}}). The bond distances associated with both ligands give further indications with regard to the trans influence of the silyl group. The Au--C bond is elongated in complex 1 compared with \([\text{IPr} \text{AuCl}]\) (from 1.942(3) to 2.091(4) Å), even more than in the hydride complex \([\text{IPr} \text{AuH}]\) (2.045(3) Å).\textsuperscript{\text{23}} The Au--Si bond of 1 (2.344(1) Å) is similar to those reported for phosphine silyl gold(1) complexes (2.354(4) to 2.3629(16) Å).\textsuperscript{\text{9,3,26,30,33}} The gold atom is strongly shielded by the flanking bulky Dipp groups of the NHCS, likely imparting kinetic stabilization to the complex.

Subsequently, the reactivity of the NHCS silyl gold(1) complex 1 toward methyl propiolate was investigated (Scheme 3). The reaction was performed in a toluene/dichloromethane (1:1) solution with an excess of alkene (10 equiv). The mixture was heated to 100 °C in a sealed vessel and monitored by \text{^{29}Si} NMR spectroscopy. Accordingly, complex 1 was found to be slowly consumed to give a new compound 2 associated with a singlet \text{^{29}Si} NMR resonance at \(\delta = 13.6\). This chemical shift is in the typical range of (vinyl)dimethylphenylsilyl groups.\textsuperscript{\text{34,35}} Complete conversion was achieved after 12 h of heating. Simple workup afforded complex 2 as a white crystalline solid in 63% isolated yield. It was characterized by NMR spectroscopy, HRMS, and X-ray crystallography.

HRMS confirmed the formation of a 1:1 adduct between complex 1 and methyl propiolate. A peculiar feature in the \text{^1H} NMR spectrum of 2 is the singlet resonance at \(\delta = 9.20\) for the vinylcyclopropane. Indeed, lower chemical shifts in the 8.0 to 8.5 ppm range were observed for the analogous products deriving from phosphine silyl gold(1) complexes.\textsuperscript{\text{5,10}} The associated \text{^{13}C} NMR signal is also much more deshielded for the NHCS complex 2 (\(\delta = 171.5\)) than for the related phosphine compounds (\(\delta = 140–145\)).\textsuperscript{\text{9,11}} It is noteworthy that the carbene signal is shifted downfield by ~20 ppm upon the reaction with methyl propiolate (from 217.4 for 1 to \(\delta = 196.7\) for 2), in line with the presence of a group with a weaker trans influence at gold.

To confirm the connectivity of complex 2 and assess its regio- and stereochemistry, an X-ray diffraction analysis was performed. The obtained molecular structure of 2 is shown in Figure 2.

Scheme 3. Reaction of Complex 1 with Methyl Propiolate

![Reaction scheme](image)

1. Dipp
2. H=\text{CO}_2\text{Me}
3. (10 eq.)
4. \text{toluene/CH}_2\text{Cl}_2
5. CO_2\text{Me}
6. Dipp
7. Au-SiMe_2Ph
8. N
9. Dipp
10. 12 h
11. 2 (65%)
syn fashion into the Au--Si bond of 1, as in the case of phosphine silyl gold(I) complexes.9,10 However, the regioselectivity is opposite to that observed with phosphines as ancillary ligands. The vinyllic proton sits in the position α to gold, meaning that the silyl and carboxyethyl groups are in gem positions to each other. A reasonable explanation for this regioselectivity may be the steric bulk of the Dipp groups of the carbene. The formed regioisomer is indeed the one minimizing steric repulsion, with the carboxyethyl group being located in the trans position to the NHCl ligand.

In summary, the first example of a silyl gold(I) complex stabilized by an NHC was synthesized and fully characterized, including by single-crystal X-ray diffraction. In contrast with analogous phosphine complexes, the presence of stericly hindered substituents at silicon is not necessary to impart stability and to enable the isolation of the complex. The NHC silyl gold(I) complex slowly reacts with methyl propiolate via migratory insertion into the Au--Si bond. The transformation is fully stereo- and regioselective. The gold and silicon atoms are added in a cis fashion (in line with a concerted inner-sphere process). The ester group is located in the trans position to the NHC ligand, minimizing the steric repulsion. These results illustrate the generality of the insertion of alkynes into Au--Si bonds. It is interesting to note that changing the ancillary substituent at gold, from a phosphine to an NHC, reverses the regioselectivity of the migratory insertion.

The silyl and vinyl gold complexes 1 and 2 stand as well-defined molecular versions of key reactive species proposed by Stratsakis to account for the silylation of alkynes catalyzed by supported gold nanoparticles.36,37 Future work from our group will aim to further extend the variety of NHC gold complexes and generalize the migratory insertion process to other Au--element bonds.

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**ABBREVIATIONS**

NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance

**REFERENCES**


(24) Kleeberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. Copper-Mediated Reduction of CO2 with pin8-SiMe3Ph via CO2 Insertion into a Copper—Silicon Bond. J. Am. Chem. Soc. 2011, 133, 19060–19063.


In a recent paper in J. Am. Chem. Soc., Schindler and co-workers reported the “Catalytic Carbonyl-Olefin Metathesis of Aliphatic Ketones: Iron(III) Homo-Dimers as Lewis Acidic Superelectrophiles”

The reaction involves cyclopentene formation, as shown below.

1) (10 points) Propose a mechanism for the reaction, utilizing a generic Lewis acid (LA) as the catalyst (we’ll get into specifics below)

2) (10 points) The methyl and benzylic groups in the alpha-position on 11 are very important in the reaction. What would happen if that position is not blocked?

3) (4 points) The first hint of what was needed was that they found quantitative yields of product using EASC as the Lewis acid. EASC (ethyl aluminum sesquichloride) is used industrially as a precursor to triethylaluminum, but is also used as a very strong Lewis acid for polymerization reactions. What’s the structure of EASC?

4) (18 points) In investigating the kinetics of the reactions, they found a rate law that is zeroth order in substrate (11) but second order in FeCl₃. On the basis of this observation, they proposed the formation of a “super-electrophile” homodimer as shown in structure 61.
a) The formation of homodimer superelectrophiles is not new, going back to at least 1969 and proposed by some very familiar names. Who originally proposed the idea of homobimetallic dimers as superelectrophiles?

b) Provide an explanation for why the homobimetallic dimer acts as a superelectrophile.

5) (50 points) The authors provide extensive spectroscopic support for their postulated homodimer, including IR, Raman and EPR.

a) One important conclusion from the Raman measurements is that the characteristic peak for FeCl₄⁻ at 330 cm⁻¹ is not observed. Discuss the significance of this conclusion (you might want to consider it in light of your answer to 4b).

b) Why was it necessary to use Raman spectroscopy to look for this vibration instead of something easier like IR?

c) The formation of FeCl₄⁻ was also ruled out by EPR. Explain how.

d) What is the geometry and electronic structure of FeCl₃?

6) (8 points) Give another example of a reaction that is catalyzed by FeCl₃ (monomer is fine, doesn’t need to be a dimer). Show the reactants, products and a mechanism.
1. (5 points each) The following questions pertain a two-level system whose ground and excited state degeneracies and energies are $g_0$, $g_1$, $\epsilon_0$, and $\epsilon_1$. You may also assume that all energies are referenced to the ground state, so that $\epsilon_0 = 0$ and thus $\Delta \epsilon = \epsilon_1 - \epsilon_0 = \epsilon_1$.

(a) Write an expression for the partition function of this two-level system in terms of $g_0$, $g_1$, and $\Delta \epsilon$.

(b) Determine the value of $g_0$ given that the partition function of this system approaches 1 in the low temperature limit.

(c) Determine the value of $g_1$ given that the partition function of this system approaches 3 in the high temperature limit.

(d) Determine the value of $\Delta \epsilon$ given that the partition function is equal to 2 at 300K.

(e) What is the probability of finding the above system in the ground state at 300K?

(f) If this two-level system represents a chemical reaction whose reactant and product species are represented by the ground and excited states, respectively, determine the equilibrium constant of the reaction at 300K?

(g) What is the entropy change for the above reaction at 300K?

(h) What is the energy change for the above reaction at 300K?

2. (5 points each) Consider a system consisting of soap (surfactant) in water in which the equilibrium concentrations of the free surfactant monomers and micelles are both equal to $\sim 10^{-3}$ M.

(a) Estimate the critical micelle concentration (or critical aggregate concentration) for this surfactant.

(b) Estimate the concentration of free (non-aggregated) surfactants in the system be when that total surfactant concentration is $\sim 10^{-4}$ M.

(c) Estimate the concentration of free (non-aggregated) surfactants in the system be when the total surfactant concentration is $\sim 10^{-2}$ M.

(d) Estimate the number of surfactants per micelle if the concentration of micelles is approximately $\sim 10^{-5}$ M when when the total surfactant concentration is $\sim 10^{-1}$ M.

(e) Sketch the aggregate size distribution as a function of the number of surfactant molecules if the polydispersity of the micelles is approximately 10% (and is consistent with your answer in question 2d).

(f) How do you expect the aggregate size distribution to change if the temperature is increased?

3. (10 points each) Reduce the following partial derivatives to an expression containing only $\alpha_P$, $\kappa_T$, $C_P$, $C_V$ and/or other thermodynamic variables.

$$\frac{\partial V}{\partial S}$$

$$\frac{\partial V}{\partial P}$$

$$\frac{\partial S}{\partial T}$$

Thermodynamic identities:

$$\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial P}{\partial T} \right)_V$$

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

$$dU = TdS - PdV$$

$$dA = -SdT - PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$