USE OF A THERMAL DESORPTION PARTICLE BEAM MASS SPECTROMETER FOR STUDIES OF SECONDARY ORGANIC AEROSOL FORMATION

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ABSTRACT

As part of a research program focusing on studies of the chemistry of gas-to-particle conversion, we have recently developed a new instrument for particle chemical analysis. This instrument, which we refer to as a thermal desorption particle beam mass spectrometer (TDPBMS), can be used for real-time, quantitative analysis of the components of organic particles, at least within the ~0.02-0.5 micrometer size range. We have also developed a temperature-programmed TDPBMS technique to aid in compound identification. Here we describe the operation of the TDPBMS and present results from our recent application of TDPBMS to studies of the chemistry of secondary aerosol formation, in which we have analyzed the composition of aerosol particles formed in environmental chamber reactions of 1-tetradecene and ozone in the presence of alcohols, carboxylic acids, and water vapor.

INTRODUCTION

Current understanding of secondary organic aerosol formation has been developed principally from environmental chamber studies of reactions of single VOCs with single or multiple oxidants. Most of these experiments have only included analyses of VOC reactants and particle size distributions, which are valuable for quantifying aerosol yield (1-4), but provide no information on chemical processes. In some experiments the chemical composition of particles collected by filtration or impaction have been determined by gas chromatography-mass spectrometry (GC-MS) of solvent-extracted components, and have provided important insight into chemical mechanisms of aerosol formation (5-8). However, while this approach yields valuable information, the technique is time consuming and is prone to sampling artifacts (9, 10). Furthermore, many of the polar and labile compounds formed are not readily amenable to gas chromatography without prior derivatization (8). The technique also does not yield the real-time information necessary to follow aerosol formation processes in detail. Therefore, although much is known about the gas-phase kinetics of the initial reactions of VOCs, and a number of studies have provided information on the volatile products and mechanisms of these reactions (11-13, and references therein), little is known about the identity of the gaseous organic products which undergo nucleation or condensation to form aerosol.

As part of a research program focusing on studies of the chemistry of gas-to-particle conversion, we have recently developed a new instrument for real-time particle chemical analysis which should help to provide some of the needed compositional information on secondary organic aerosols. We have demonstrated that this instrument, which we refer to as a thermal desorption particle beam mass spectrometer (TDPBMS), can be used for real-time, quantitative analysis of the components of organic particles, at least within the ~0.02-0.5 µm size range (14). We have also developed a temperature-programmed TDPBMS technique (TPTD) to aid in compound identification (15). Here we describe the TDPBMS we have constructed and present the results of detailed characterization studies which are necessary for understanding the performance of the instrument. We also describe techniques we have developed for accurately calibrating the instrument for quantitative analysis of organic particles, and the TPTD technique for compound identification. Use of the TDPBMS for aerosol analysis is demonstrated in an environmental chamber study of the chemistry of secondary aerosol formation from reaction of 1-tetradecene and ozone in the presence of 2-propanol.

EXPERIMENTAL

Aerosol Mass Spectrometric Analysis by TDPBMS and TPTD. Detailed descriptions of the TDPBMS and its operation for real-time analysis (14) and temperature-programmed thermal desorption (TPTD) (15) are presented elsewhere. The TDPBMS and associated apparatus are shown in Figure 1. Aerosol is sampled into the TDPBMS through a 100 µm orifice, which maintains the flow at 0.075 L/min and reduces the pressure from atmospheric to ~2 torr. Particles then enter a tube containing a series of aerodynamic lenses (16, 17), which focus the particles into a very narrow, low-divergence particle beam that transports ~0.02-0.5 µm particles from atmospheric pressure into the high-vacuum chamber with near-unit efficiency. The operation of the lenses is simulated in Figure 2 for gas molecules and particles. After exiting the aerodynamic lens nozzle, particles pass through two flat-plate skimmers separating three differentially-pumped chambers and enter the detection chamber where the pressure is ~5 x 10^{-8} torr. The vacuum is maintained by turbomolecular pumps mounted on each chamber and backed by an oil-free mechanical pump to reduce contaminating organic vapors in the system. Inside the detection chamber particles impact on the walls of a V-shaped molybdenum foil (volume ~0.1 cm^3), which is either resistively heated continuously at 165 ± 3 ^{o}C for real-time TDPBMS analysis or cooled to -50°C by an external liquid nitrogen bath for collection of particles for TPTD. The vaporization cell temperature is monitored by an attached thermocouple and regulated by a temperature controller. After vaporization the molecules diffuse into an ionizer where they are impacted by 70 eV electrons, and the resulting ions are mass analyzed in a quadrupole mass spectrometer (Extrel MEXM 500, 1-500 amu mass range) equipped with a conversion dynode/pulse counting detector.

Particle analysis by TPTD is carried out on ~1 µg of aerosol collected on the cryogenically-cooled vaporizer. Samples are desorbed by heating at a ramp rate of ~1°C/min for about two hours, while mass spectra are continuously recorded. During TPTD the aerosol components desorb according to their vapor pressures, so mass spectra of individual compounds can be extracted from time-dependent mass spectra.

Aerosol Generation and Environmental Chamber Technique. Organic aerosols of desired compositions used for instrument characterization were generated using a Collison atomizer. An ~0.1% (w/w) solution of the organic compounds in 2-propanol was atomized to a mist using clean air and sent through a diffusion drier to evaporate the alcohol solvent. The aerosol then flows through a bipolar charger and differential mobility analyzer (DMA) (18) to obtain near-monodisperse, size-selected particles for our experiments. Particles used here were ~0.15 µm in diameter. Particle concentrations were measured using an aerosol electrometer.

The products of the liquid- and gas-phase reactions of 1-tetradecene and ozone in the presence of 2-propanol were also analyzed by TPTD. The reaction was conducted in the liquid-phase by bubbling a 1.5 L/min flow of 2% O_3/O_2 through a 2% (w/w) solution of 1-tetradecene in 2-propanol for 2 hours. The reacted solution was then used to create a monodisperse aerosol as described above. The gas-phase reaction leading to formation of secondary organic aerosol was carried out in an ~7000 L Teflon environmental chamber filled with clean air and 0.3 ppm 1-

tetradecene, 1.3 ppm ozone, and 2000 ppm 2-propanol. The propanol scavenges >95% of the OH radicals formed in the reaction (19), thereby simplifying the aerosol products by eliminating reactions between 1-tetradecene and OH. After one hour of reaction, aerosol consisting of ~0.1-0.3 mm sized aerosol particles was sampled for ~20 min into the TDPBMS without size selection for cryogenic collection and subsequent TPTD.

RESULTS AND DISCUSSION

Particle Sampling and Vaporization. In order to calibrate the TDPBMS for quantification of organic compounds it is necessary to characterize particle transport and vaporization in the instrument. The efficiencies with which particles are sampled from atmospheric pressure and transported into the unheated vaporization cell in the TDPBMS was evaluated in a series of measurements using monodisperse aerosol particles of various sizes and compositions. The results of these experiments are shown in Figure 3. The stated diameters are for singly charged particles, but there is a small contribution (less than 5%) to the measurements from larger, doubly and triply charged particles. Over the range of particle diameters from 0.02-0.5 µm the transport efficiencies were greater than 40% for all particles, but differed with particle size and composition. The efficiency is a reflection of the width of the particle beam, with wider beams having lower efficiencies because of particle losses at the skimmers and the entrance to the vaporization cell. Particle losses are small between the DMA and the particle beam lens. The decrease in efficiency with decreasing particle size is due to broadening of the beam by Brownian motion of the particles in the lenses and nozzle, and the decrease at larger particle sizes is probably due to decreased focusing efficiency by the lenses. Particle composition influences the efficiency through its effect on particle shape. Lift forces acting on nonspherical particles during nozzle accelerations cause broadening of the particle beam (16, 17), therefore, the efficiencies are highest for spherical and highly symmetric particles, and lower for those with irregular shapes (20). The highest efficiencies measured here were for dioctyl sebacate (DOS) [-$(CH_2)_4CO_2CH_2CH(C_2H_5)CH_2)_3CH_3]_2$ particles, since they are liquid drops. Glutaric acid [$HOOC(CH_2)_3COOH$], which is a solid dicarboxylic acid, also has high efficiencies, suggesting a spherical or regular shape. The lowest efficiencies were measured for palmitic acid [$CH_3(CH_2)_{14}COOH$], which is a solid, long-chain monocarboxylic acid that apparently forms irregularly shaped particles. However, the presence of DOS in a 1:1 mixture with palmitic acid leads to a more spherical particle, as reflected in the increased efficiencies. The efficiency curve for adipic acid [$HOOC(CH_2)_4COOH$], which is also a solid dicarboxylic acid, increases with particle size to physically impossible values higher than 100%. For particles larger than those shown in Figure 3 they go well off scale. The reason for this is that some of the particles are bouncing out of the vaporization cell with a charge that is different from when they entered, resulting in an apparent transport efficiency greater than 100%. The effect of bounce on these measurements increases with increasing particle size because larger particles bounce more readily, and they can carry away more charge. As one might expect, when adipic acid is mixed with an equal mass of DOS, the measured efficiencies become more reasonable and are close to those of a liquid drop, indicating that the DOS prevents the particles from bouncing and makes the particle more spherical.

Although hard, crystalline particles such as $(NH_4)_2SO_4$ and adipic acid can bounce out of an unheated vaporization cell, mass spectrometric measurements made with a heated cell demonstrate that particles completely vaporize before bouncing out. This can be seen from the data in Figure 4, which show the mass spectral signal measured for a constant current of monodisperse DOS and $(NH_4)_2SO_4$ particles of various sizes (the quantity plotted in Figure 4 is actually an “effective” single-particle volume that has been corrected for contributions from larger, multiply-charged particles). The linear relationship is indicative of complete evaporation, since bounce and incomplete evaporation would increase with particle size, leading to a less than linear increase in mass spectral signal with increasing particle volume.

Particle Mass Spectral Analysis: Compound Quantification and Identification. Quantification of a compound present in an air sample requires the determination of a relationship between the mass spectral signal and the mass concentration of the compound (e.g. $\mu g/m^3$ of air). In the ideal case that the calibration and sample particles are spherical, the calibration curve would be similar to those shown in Figure 4, where the upper x-axis gives the mass concentration of particulate compound calculated for a measured input concentration of single-component, monodisperse particles obtained from the atomizer and DMA [both DOS and $(NH_4)_2SO_4$ particles are spheres]. If the calibration particles are not spherical, then the calculated mass concentration will be in error. For organic compounds that are solids, and may therefore form nonspherical particles, a low vapor pressure organic liquid such as DOS or oleic acid [$CH_3(CH)_7CH{=}CH(CH_2)_7COOH$] can be added to the atomizer solution to create multicomponent spherical particles. The mass concentration of the compound of interest can then be calculated from the relative concentration of solutes. However, this approach requires that the mass spectrometer signal not depend on the particle matrix, but only on the quantity of calibration compound present in the particles. The data shown in Figure 5, which are the results of mass spectral measurements made on pure and multicomponent particles, demonstrate that this is the case for the TDPBMS. For mixed DOS/oleic acid (liquid/liquid) and DOS/tridecanoic acid (liquid/solid) particles, the signal measured per mass of compound sampled (uncorrected for transport efficiency) for the multicomponent particles is within ~5-10% of the pure particle signal, regardless of the composition. This result is reasonable, since as long as the particles evaporate completely, have similar transport efficiencies, and have spherical shapes, then the signal obtained when a given mass of compound is sampled into the instrument should be the same for pure and multicomponent particles. The transport efficiencies of 0.1 µm DOS/oleic acid and 1:1 DOS/tridecanoic acid particles are 100% and 95%, respectively, indicating that both types of particles are spherical or nearly spherical in shape.

Once a calibration curve such as those shown in Figure 4 is determined using spherical particles, the mass spectral signal can be used to determine the concentration of compound present in an air sample by multiplying the concentration obtained from the calibration curve by the ratio of the transport efficiencies of sample and calibration particles. Based on the uncertainties in the measured quantities we estimate a total uncertainty in the concentration of ~20%. This value is quite acceptable for our application of the technique, but as we show below, attaining this level of accuracy in environmental chamber studies will depend on our ability to associate mass spectral peaks with particular compounds present in particles.

Multicomponent Aerosol TPTD. The basis for using mass spectrometry for chemical analysis of particles is that each compound has a unique mass spectrum, “a fingerprint,” which can be compared with a particle mass spectrum to determine if the compound is present in the particle. However, the TDPBMS mass spectra of the environmental chamber particles we analyze are a composite of the mass spectra of all the individual particle components, as is shown in Figure 6 for a reaction of 1-tetradecene and ozone. For this reason we developed a TPTD technique for extracting single-compound information. During TPTD the aerosol is collected and then slowly heated so that components desorb according to their vapor pressures. Mass spectra of individual compounds can then be extracted from time-dependent mass spectra. Figure 7 depicts example mass thermograms for two-component (A) and three-component (B) test aerosols. Thermogram B resulted from a mixed aerosol of adipic acid, DOS, and stearic acid [$CH_3(CH_2)_{16}COOH$] analyzed using a temperature ramp of ~0.75°C/min. For this mixture, *m/z*

100, 185, and 284 are specific markers for adipic acid, DOS, and stearic acid, respectively, and indicate that these compounds thermally desorb over 10-20 minutes at this ramp rate. This is reflected in the *m/z* signal traces, which in this case have well-resolved maxima. If these were unknown compounds, it would be obvious that *m/z* 100, 185, and 284 should be assigned to three different mass spectra. The *m/z* 60 signal would be assigned to the same mass spectra as *m/z* 100 and 284. Thermogram A shows similar results for a two-component aerosol consisting of glutaric acid [$HOOC(CH_2)_3COOH$] and DOS.

Our data reduction technique allows the creation of single-compound mass spectra from all *m/z* signals bracketed within user-specified time or temperature ranges, which can be visually determined from mass thermograms (Figure 7) or plots of peak desorption temperatures (or times) versus *m/z*, as illustrated in Figure 8. Figure 9 presents examples of the mass spectra of glutaric acid (A) and DOS extracted from the TPTD analysis of the two-component aerosol, which match the spectra available for these compounds in the Wiley Database (not shown). The spectra acquired for pure glutaric acid (B) and DOS (D) using the continuous vaporization mode of TDPBMS, which are similar to the respective Wiley Database spectra, are shown in Figure 9 for comparison. These examples demonstrate how TPTD can be used to extract many of the fragment ion peaks associated with an individual compound present in a mixture, and create a mass spectrum for use in compound identification. Although mass thermogram peak shapes are generally broad, component mass spectra can still be extracted as long as there is adequate separation of peak maxima. The limitations of TPTD for compound separation were investigated by analyzing aerosol mixtures comprised of components with various degrees of vapor pressure differences at different temperature ramp rates. The results indicate that a minimum time separation of ~4 minutes (or ~3-4^{o}C) at temperature ramp rates of <1^{o}C/min is needed to extract accurate mass spectra for equal-mass mixtures of compounds, as is shown for DOS and stearic acid in Figure 7B. This 3-4°C temperature separation corresponds to approximately a factor of 5 difference in room temperature vapor pressure. This performance is sufficient to separate compounds in a homologous series of monocarboxylic acids or *n*-alkanes, where each additional CH_2 unit introduces approximately a factor of 5 decrease in vapor pressure.

TPTD of Ozone-Alkene Reaction Products. The aerosol generated from the gas-phase reaction of 1-tetradecene [$CH_3(CH_2)_{11}CH=CH_2$] with ozone in the presence of excess 2-propanol was sampled from an environmental chamber to demonstrate the utility of TPTD in laboratory studies. After collection of polydisperse aerosol, TPTD at ~1.3°C/min resulted in the separation and identification of two compounds that desorbed at 24°C and 38°C (Figure 10). The mass spectra are presented in Figure 11. The higher vapor pressure aerosol component that desorbed first (A) was identified as tridecanoic acid by comparison with the Wiley Database spectra (not shown) and the pure tridecanoic acid TDPBMS spectra (B), and is an expected product of this reaction. Mechanisms of the liquid- and gas-phase reactions of ozone with alkenes have been reported (21, 22), and for 1-tetradecene, ozone adds to the >C=C< bond to yield an energy-rich primary ozonide as depicted in Figure 12. This ozonide then decomposes to create formaldehyde and an energy-rich Criegee biradical. Tridecanoic acid is formed by rearrangement of the excited biradical. Although the ozonide can also decompose to tridecanal and a one-carbon biradical, this pathway leads to products that are too volatile to form aerosol. A second, slightly less volatile component (Figure 11C) was found using TPTD, but the extracted mass spectrum had no satisfactory match in the Wiley Mass Spectral Database. However, based on the results of recent gas-phase studies on ethene (22), and liquid-phase studies on numerous other alkenes (21, 23, 24), it is expected that the major product of ozonolysis of 1-tetradecene in the presence of excess 2-propanol will be α-isopropoxytridecyl hydroperoxide formed by the mechanism shown in

Figure 12. This compound would most likely have a lower vapor pressure than tridecanoic acid, conforming with the TPTD results.

To test this hypothesis, a solution of 1-tetradecene in 2-propanol was ozonated and the product solution was atomized and analyzed by TDPBMS. The liquid-phase reaction is known to produce α-alkoxyalkyl hydroperoxides in near-quantitative yield (23), so the excellent agreement between the TPTD spectrum of chamber aerosol and the liquid-phase mass spectrum (Figure 11D) is strong evidence that compound B is α-isopropoxytridecyl hydroperoxide. It is worth noting that hydroperoxides such as this may not be amenable to GC analysis (we have observed that they thermally decompose) and would therefore be overlooked using traditional GC-MS identification procedures. Moreover, this environmental chamber analysis serves as one example where TPTD is successful in identifying two aerosol components present in concentrations differing by approximately an order of magnitude.

CONCLUSIONS

The results of this work demonstrate that the thermal desorption particle beam mass spectrometer (TDPBMS) we have developed can be used for quantitative, real-time measurements of organic compounds present in secondary aerosol formed in a laboratory environment. The TDPBMS is capable of analyzing particles between ~0.02-0.5 µm as long as the mass concentration of the compound is greater than ~0.1-1 $\mu g/m^3$, but this size range can be extended in both directions for higher concentrations. The estimated uncertainty in concentration measurements is ~20%. The instrument can be calibrated using monodisperse aerosol particles of known composition, size, and concentration, generated using an atomizer and differential mobility analyzer. Because the mass spectral signal measured for a given mass of a particular compound is independent of the presence of other compounds in the particle, calibrations can be performed using pure or multicomponent particles. However, calibrations will be most accurate when the particles are spherical, since this allows a more accurate calculation of the particle mass from the measured mobility diameter. When calibrating with solid compounds, which can form nonspherical particles, it is preferable to mix the compound of interest with a low vapor pressure organic liquid such as DOS or oleic acid to make spherical, multicomponent particles. Quantification by TDPBMS is currently limited to species with vapor pressures less than ~10^{-5} torr, since particle evaporation introduces error in the measurement.

The TPTD technique presented here is potentially a powerful tool for identification of aerosol components in environmental chamber studies of atmospheric chemistry, and complements the quantitative TDPBMS methods. When compared to other analytical methods, this procedure minimizes sample handling since aerosol is sampled directly into the analysis chamber over a few minutes, and reduces the possibility for decomposition of unstable reaction products since evaporation is accomplished at low temperatures in a high-vacuum chamber. When analyzing aerosols of equal-mass mixtures of compounds, a vapor pressure difference of a factor of 5 or more at a temperature ramp rate of ~0.75°C/min gives sufficient separation for accurate mass spectral identification. This is adequate resolution for many applications since, for example, there is approximately a factor of 5 decrease in vapor pressure for each additional CH_2 unit in a homologous series of monocarboxylic acids (neglecting odd-even differences in vapor pressure) or *n*-alkanes. When used alongside TDPBMS, TPTD can provide valuable information in the study of the chemistry of secondary organic aerosol formation.

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REFERENCES

(1) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; John Wiley & Sons; New York, 1998.

(2) Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol*. **1996**, 30, 2580.

(3) Odum, J. R. Jungkamp; T. P. W., Griffin, R. J.; Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol.* **1997**, 31, 1890.

(4) Hoffman, T.; Odum, J. R.; Bowman, F.; Collins, D.; Klockow, D.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem*. **1997**, 26, 189.

(5) Grosjean, D. In *Ozone and Other Photochemical Oxidants*; Chapter 3, National Academy of Sciences: Washington DC, 1977; pp. 45-125.

(6) Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol*. **1997**, 31, 1345.

(7) Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. *Atmos. Environ*. **1997**, 31, 1953.

(8) Yu, J.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol*. **1998**, 32, 2357.

(9) Ligocki, M. P.; Pankow, J. F. *Environ. Sci. Technol*. **1989**, 23, 75.

(10) McDow, S. R.; Huntzicker, J. J. *Atmos. Environ*. **1990**, 24A, 2563.

(11) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, Monograph 1, 1.

(12) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, Monograph 2, 1.

(13) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, 26, 215.

(14) Tobias, H. J.; Kooiman, P. M.; Docherty, K. S.; Ziemann, P. J. *Aerosol Sci. Technol.* **1999**, in press.

(15) Tobias, H. J.; Ziemann, P. J. *Anal. Chem.* **1999**, 71, 3428.

(16) Liu, P.; Ziemann, P. J.; Kittelson, D. B.; McMurry, P. H. *Aerosol Sci. Technol*. **1995**, 22, 293.

(17) Liu, P.; Ziemann, P. J.; Kittelson, D. B.; McMurry, P. H. *Aerosol Sci. Technol*. **1995**, 22, 314.

(18) Kinney, P.D.; Pui, D.; Mullholland, G.W.; Bryner, N.P. *J. Res. Natl. Inst. Stand. Technol*. **1991**, 96, 147.

(19) Atkinson, R.; Ashmann, S.M.; Arey, J.; Shorees, B. *J. Geophys. Res*. **1992**, 97, 606.

(20) Ziemann, P. J.; Kittelson, D. B.; McMurry, P. H. *J. Aerosol Sci*. **1996**, 27, 587.

(21) Bailey, P.S. in *Ozonation in Organic Chemistry*, Volume 1, Academic Press: London, 1978.

(22) Neeb, P.; Horie, O.; Moortgat, G.K. *Int. J. Chem. Kinetics* **1996**, 28, 721.

(23) Zelikman, E. S.; Yur’ev, Y. N.; Berezova, L. V.; Tsyskovskii, V. K. *J. Org. Chem. USSR* (*Engl. Transl*.) **1971**, 7, 641.

(24) Pospelov, M. V.; Menyailo, A. T.; Bortyan, T. A.; Ustynyuk, Yu. A.; Petrosyan, V. S. *J. Org. Chem. USSR* (*Engl. Transl*.) **1973**, 9, 312.