

Vapor Pressure Measurements on Low-Volatility Terpenoid Compounds by the Concatenated Gas Saturation Method

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The atmospheric oxidation of monoterpenes plays a central role in the formation of secondary organic aerosols (SOAs), which have important effects on the weather and climate. However, models of SOA formation have large uncertainties. One reason for this is that SOA formation depends directly on the vapor pressures of the monoterpene oxidation products, but few vapor pressures have been reported for these compounds. As a result, models of SOA formation have had to rely on estimated values of vapor pressure. To alleviate this problem, we have developed the concatenated gas saturation method, which is a simple, reliable, high-throughput method for measuring the vapor pressures of low-volatility compounds. The concatenated gas saturation method represents a significant advance over traditional gas saturation methods. Instead of a single saturator and trap, the concatenated method uses several pairs of saturators and traps linked in series. Consequently, several measurements of vapor pressure can be made simultaneously, which greatly increases the rate of data collection. It also allows for the simultaneous measurement of a control compound, which is important for ensuring data quality. In this paper we demonstrate the use of the concatenated gas saturation method by determination of the vapor pressures of five monoterpene oxidation products and *n*-tetradecane (the control compound) over the temperature range 283.15–313.15 K. Over this temperature range, the vapor pressures ranged from about 0.5 Pa to about 70 Pa. The standard molar enthalpies of vaporization or sublimation were determined by use of the Clausius–Clapeyron equation.

Introduction

Globally, vegetation emits a tremendous quantity of volatile organic compounds (VOCs) (1–5). Annually, plants and trees emit more than 10^{12} kg of carbon as VOCs, about 40% of which is isoprene (2–5). The balance of these emissions is mostly monoterpenes such as α - and β -pinene. In the atmosphere, monoterpenes are readily oxidized to less volatile “monoterpenoid” compounds, which then form aerosols (1, 5–8). Such secondary organic aerosols (SOAs) have an important impact on climate because of the way that they scatter and absorb solar radiation, and because of

their role in cloud formation (1, 9). However, there is still substantial uncertainty associated with the treatment of SOAs in global climate models. For example, SOA formation depends directly on the vapor pressures of the constituent compounds (1, 9, 10), but only a few vapor pressure measurements have been made on these compounds (1, 8, 11–14). Consequently, models of aerosol formation have to rely on estimated values of vapor pressure for aerosol precursors (9). For this reason, a recent review of organic aerosols and global climate modeling concluded that accurate measurements of vapor pressure (and enthalpy of vaporization/sublimation) are needed in order to decrease the uncertainty in global climate models (1).

The lack of known vapor pressures for monoterpene compounds illustrates a broader need for vapor pressure measurements on low-volatility compounds for scientific and environmental applications (15–17). Typically, for organic compounds with high molar mass, the best one can hope to find in the literature is a single measurement at high temperature (such as a boiling temperature). Even when a high temperature measurement has been reported, it often has a large uncertainty because of thermal decomposition or other reasons, which can force a reliance on group contribution estimates (18).

The vapor pressures of compounds of high molar mass are typically less than 1 kPa at temperatures below 323 K (the temperature range of greatest concern for environmental and climate studies), which limits the number of useful vapor pressure measurement methods (16, 19). Methods that directly measure the pressure exerted by the vapor phase (e.g., static gauged bombs and ebulliometry) are often not suited to measurements on low-volatility samples for multiple reasons. First, the contributions of volatile impurities to measured pressures can be significant at extremely low impurity mole fractions (19, 20). The reason, of course, is that impurities can have vapor pressures that are orders of magnitude greater than that of the sample compound. Second, these methods typically require sample masses of at least a few grams. Obviously, large amounts of highly pure material are difficult to obtain for many compounds of environmental interest.

A variety of “indirect” methods are capable of measuring the vapor pressures of low-volatility compounds (11–14, 16, 21–27). However, the gas saturation method and the effusion method (when high-purity samples are available) are generally considered to be the most accurate of these methods for low vapor pressures (16). The gas saturation method (16, 19–21, 28–32) is a simple technique that involves the saturation of a carrier gas stream with the vapor of a condensed phase of the compound of interest. The most common approach is to strip the vapor from a measured volume of the saturated carrier gas using an adsorber or cold trap, and then measure the recovered mass with an appropriate analytical method. The vapor pressure is then calculated with the ideal gas equation, eq 1,

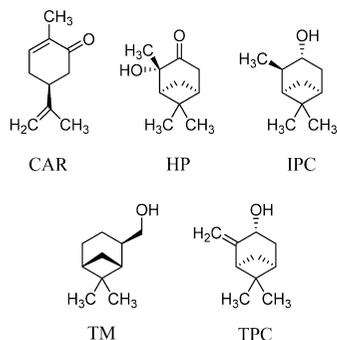
$$p_{\text{sat}} = (m \cdot R \cdot T) / (V \cdot M) \quad (1)$$

where p_{sat} is the vapor pressure, m is the recovered mass of the vapor, R is the gas constant, T is the temperature of the saturator, V is the volume of carrier gas at the temperature and pressure of the saturator, and M is the molar mass of the compound.

The gas saturation method has several key advantages (16, 21, 27, 28). Calibration is not required. Impurities have a relatively small effect on the measured vapor pressures,

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SCHEME 1. Chemical Structures and Abbreviations for the Monoterpenoids Studied



assuming that a technique such as gas chromatography is used to determine the amount of solute vapor, so samples of limited purity can be used. Little sample is needed for a measurement (typically tens of milligrams or less), again assuming that a sensitive analytical method is used to determine the amount of vapor. Finally, such an apparatus is simple and inexpensive to build and operate. On the other hand, traditional gas saturation methods have two significant drawbacks. First, measurement periods can be quite long if a large volume of carrier gas is needed in order to collect a sufficient amount of vapor for analysis. Second, the method is susceptible to certain types of systematic errors (e.g., leaks) that can be difficult to detect.

The “concatenated” gas saturation method (21) was developed in order to compensate for the drawbacks mentioned above. In this type of apparatus, several saturator-adsorber pairs are linked in series, so that multiple measurements can be made simultaneously with the same carrier gas stream. This approach greatly speeds data collection. It also allows for strategies that ensure data quality. For example, a control compound with a well-known vapor pressure can be measured simultaneously with the sample compounds. If the measurement yields the expected vapor pressure for the control compound, one has a high level of confidence in the other measurements that were made simultaneously.

The concatenated gas saturation method can make a valuable contribution to vapor pressure measurements on environmentally important compounds. By use of a recently constructed apparatus with 18 saturator-adsorber pairs, we demonstrate the utility of the method with a series of monoterpenoid compounds. The monoterpenoids were (+)-carvone (CAR), (1*S*,2*S*,5*S*)-(-)-2-hydroxy-3-pinanone (HP), (1*R*,2*R*,3*R*,5*S*)-(-)-isopinocampheol (IPC), (+)-*trans*-myrtanol (TM), and (-)-*trans*-pinocarveol (TPC). Scheme 1 shows the chemical structures of the monoterpenoids and the abbreviation used for each. The vapor pressures of these compounds, as well as *n*-tetradecane (the control compound), were measured over the temperature range 283.15–313.15 K.

Experimental Section

Chemicals. Reagent-grade acetone, used as a solvent in this work, was obtained from a commercial source and used as received. It has a stated purity of 99.5%, which is consistent with our own routine analyses of such solvents by gas chromatography (33). The *n*-tetradecane and monoterpenoids were obtained from commercial sources and used as received. The stated purities of these compounds are 99% for *n*-tetradecane, 98.5% for CAR, 99% for HP, 98% for IPC, 98.5% for TM, and 96% for TPC. Sulfur hexafluoride (SF₆), used as the carrier gas, was obtained from a commercial source with a purity of 99.9%. Before use, the SF₆ was transferred into an aluminum

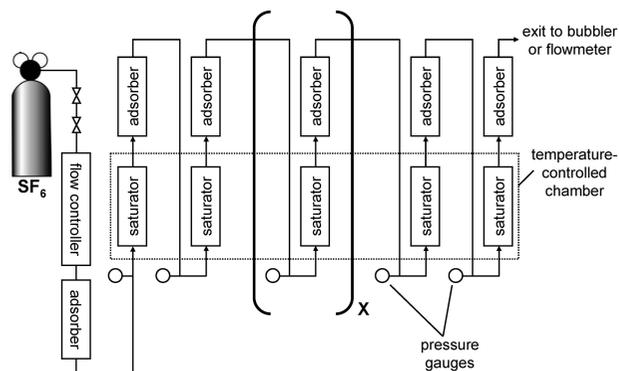


FIGURE 1. A concatenated gas saturation apparatus featuring several saturator-adsorber pairs linked in series. The apparatus used for this study has 18 saturator-adsorber pairs ($X = 14$).

cylinder to facilitate mass determinations. SF₆ was chosen as the carrier gas for a variety of reasons: it is inert, it is less prone to leak than gases like nitrogen or argon, diffusion in SF₆ is relatively slow (mass transfer by diffusion is undesirable in this system), and its high density facilitates mass determinations (see below).

Concatenated Gas Saturation Apparatus. The apparatus used for these measurements was designed and constructed at NIST. A detailed description of the apparatus is published in a recent paper (34), so only an overview of the principal components is given here. It is also worth noting that this apparatus is similar to an earlier apparatus for which a detailed description has also been published (21). The principal components of the apparatus are illustrated schematically in Figure 1. The carrier gas supply includes an aluminum gas cylinder, pressure regulator, and flow controller. The cylinder-regulator assembly must be removed between measurements to determine the mass of carrier gas that was used. To facilitate this procedure, it is connected to the flow controller by a short stainless steel capillary with a valve at each end. Closing these two valves allows the cylinder-regulator assembly to be removed with the loss of only the capillary's volume of carrier gas (approximately 1 mg of SF₆). Carrier gas from the flow controller first passes through an adsorbent column packed with the porous polymer adsorbent poly(2,6-diphenyl-1,4-phenylene oxide) (33, 35–37). The gas then flows through the 18 saturator-adsorber pairs. The saturators are located inside a forced-air, temperature-controlled chamber and consist of PTFE tubes (1 m in length with an inside diameter of 0.48 cm) filled with glass beads with a diameter of 0.3 cm. The adsorbers, which are removable, are located on a manifold above the chamber (at room temperature, approximately 21 °C) and consist of stainless-steel tubes (7.5 cm in length with an inside diameter of 0.86 cm) packed with poly(2,6-diphenyl-1,4-phenylene oxide). A stainless steel capillary tube attached to the inlet end of each adsorber penetrates through the wall of the temperature-controlled chamber and into the end of the saturator, which prevents the loss of vapor as the carrier gas flows from the temperature-controlled saturator to the room-temperature adsorber. Between each saturator-adsorber pair, a Bourdon tube pressure gauge displays the pressure. At the end of the saturator-adsorber series, the carrier gas flows through a flowmeter or an indicating bubbler before it is expelled at ambient pressure. The flowmeter and bubbler are used for diagnostic purposes only, to set the flow rate to an approximate value or to verify the flow of carrier gas at a glance.

Vapor Pressure Measurements. First, each saturator was coated with one of the monoterpenoids or with *n*-tetradecane.

This was done by wetting the saturator with a 10% solution of one of the compounds in acetone, and then removing the acetone by gently flowing helium through the adsorber at room temperature for 0.5 h. Approximately 1 mL of solution was used to wet each saturator, which means that approximately 0.1 g of the compound was deposited. Given the surface area of the saturator (approximately 0.024 m²), we estimate that the average thickness of the coating was 4 μm. The saturators were then installed in the temperature-controlled chamber of the apparatus. The saturators had to be coated only once for all of the vapor pressure measurements because no more than 8 mg of any compound evaporated from a saturator during a measurement.

Before starting a measurement, the SF₆ supply cylinder was weighed on a 25 kg two-pan balance with a sensitivity of 2.5 mg. In order to eliminate a buoyancy correction, an evacuated ballast cylinder was placed on the other balance pan (along with class S standard weights). We used a large supply cylinder to avoid frequent refills (and because we have a balance capable of weighing it); however, a much smaller supply cylinder would also work because the amount of SF₆ used for each measurement is relatively small (no more than 65 g for this work). After weighing, the SF₆ cylinder was connected to the gas saturation apparatus and the adsorbers were also installed. The temperature was set and, after thermal equilibration, the flow of SF₆ was initiated. The flow rate of carrier gas was between 0.4 and 0.5 L per day, which means that the residence time of the carrier gas in a saturator was approximately 0.5 h. Flow times ranged from 5 days (at 313.15 K) to 40 days (at 283.15 K). The atmospheric pressure was logged at regular intervals in order to obtain an average atmospheric pressure for the measurement.

Upon passage of a sufficient quantity of carrier gas, the flow of SF₆ was stopped and the cylinder weighed again. Each adsorber was removed from the apparatus and eluted with acetone. The elution was done with a syringe pump set to deliver acetone at a rate of 0.25 mL/min. The eluent from each adsorber was collected into two vials. The first 5 mL of eluent was collected in the first vial, and it typically contained almost all of the detectable solute. The next 5 mL of eluent was collected in the second vial, and it never contained more than 3% of the recovered solute. This method ensures that all detectable solute has been stripped from the adsorber. After elution, the adsorbers were dried with a flow of warm helium before using them for the next vapor pressure measurement. The unmanipulated eluent fractions were analyzed by gas chromatography with flame ionization detection (GC-FID). Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was used in the splitless mode and maintained at 250 °C. The samples were separated on a 30 m capillary column coated with a 0.1 μm film of (5%-phenyl)-methylpolysiloxane. The moderate polarity of monoterpenoids gives a somewhat poor peak shape on this stationary phase, but the monoterpene peaks were well separated from the solvent peaks. The temperature program was 1 min at 50 °C, followed by a 100 °C/min gradient to 65 °C, followed by a 10 °C/min gradient to 150 °C.

The mass change of the supply cylinder was used to calculate the amount of SF₆ used for each measurement. The volume of carrier gas, V in eq 1, at the experimental temperature and average atmospheric pressure, was then calculated by use of an equation of state for SF₆ that is explicit in Helmholtz energy (38), as implemented in REFPROP (39). The mass of vapor collected in the adsorber, m in eq 1, was determined by calibrated gas chromatography, as described above.

Avoiding Systematic Errors in the Measurement of p_{sat} . With the gas saturation technique there are several potential

pitfalls that can cause systematic errors in p_{sat} . For the concatenated apparatus used herein, which has a large number of connections along the carrier gas stream, a likely source of error is a leak. Downstream from a leak, less carrier gas is flowing through the apparatus than one assumes (at least, that is the case with our method of determining carrier gas flow by mass). This means that less-than-expected amounts of solute are carried into the adsorbers, resulting in values of p_{sat} that are systematically low. We employed three strategies for guarding against leaks. First, the apparatus was thoroughly leak-checked before any measurements were made. Second, simultaneous measurements on each compound were done in triplicate, and these measurements were spaced along the apparatus in a particular way. For example, CAR was measured with the 4th, 10th, and 16th saturator-adsorber pairs. This way, comparisons of p_{sat} measured in different parts of the apparatus can be used to detect (and even pinpoint) leaks that occur within the saturator-adsorber chain. Third, the p_{sat} of a control compound, *n*-tetradecane, was measured at the same time as the monoterpenoids using the 6th, 12th and 18th saturator-adsorber pairs. Thus, if the sixth saturator-adsorber pair yields the expected value of p_{sat} for *n*-tetradecane, one can assume that the measurements made with the first through fifth saturator-adsorber pairs were unaffected by a leak. This arrangement makes it possible to retain any good measurements, even if there is a leak somewhere downstream. Spacing the samples in this way also allows one to detect inefficient trapping by carry-over to the next adsorber (something that was not observed during these measurements). It should be noted that we saw no evidence of a leak anywhere in the system during these measurements.

Some other possible sources of systematic error are inefficient trapping of the sample vapor in the adsorbers, incomplete elution of a sample from the adsorbers, insufficient analytical sensitivity when determining the amount of sample in the eluent, a carrier gas flow rate that is too fast, and decomposition of a sample during the measurement. The successful measurements on *n*-tetradecane provide direct evidence against several of these. Efficient sample trapping was demonstrated by the lack of sample carry-over (see above). This was anticipated because this type of adsorber has been found to be at least 99.99% efficient for other polar organic compounds (21). The elution procedure is specifically designed to ensure that all detectable solute has been stripped from the adsorber. Calibration curves show that GC-FID is sufficiently sensitive in the range of these experiments. The carrier gas flow rate was only about 0.5 L per day, which means that the residence time of the carrier gas in a saturator is 0.5 h. This is important because it allows ample time for the vapor phase to become saturated with solute, and it decreases the driving force for physically carrying the condensed phase into the adsorbers. We did observe apparent decomposition of one monoterpene that we tried to measure, (1S)-(-)-verbenone, so no data are reported for that compound.

Uncertainties in the Measurement of Vapor Pressure. A detailed description of the uncertainties in the measurement of vapor pressure with this apparatus is published elsewhere (34) so only a summary is given here. The combined relative standard uncertainty for the method and apparatus is estimated to be 7%, and is due primarily to uncertainties in the experimental temperature and pressure, and to uncertainty in the GC analysis (34). There are also uncertainties caused by impurities in the monoterpenoids and with the use of the ideal-gas law (eq 1) (34). In an ideal-mixture approximation, the partial pressure of the major component of a sample is equal to the product of its mole fraction and its vapor pressure. The mass-fraction purity of the monoterpenoids and *n*-tetradecane ranges from 0.96 to

TABLE 1. Comparison of p_{sat} Reference Data for n -Tetradecane with p_{sat} Determined by the Concatenated Gas Saturation Method

T (K)	TDE	TDE	gas saturation	gas saturation
	p_{sat} (Pa)	uncertainty (Pa)	p_{sat} (Pa)	uncertainty (Pa)
283.15	0.401	0.016	0.427	0.060
293.15	1.15	0.04	1.21	0.17
303.15	3.01	0.09	3.22	0.45
313.15	7.32	0.19	8.10	1.13

0.99 (see above). It is likely that the average molar mass of the impurities is similar to the molar masses of the sample compounds; in that case, the mole fraction purities of the sample compounds also range from 0.96 to 0.99, which would result in a 1–4% shift in the measured vapor pressures. In a similar way, solubility of the carrier gas in a liquid phase can shift the measured vapor pressures. The mole fraction solubility of SF₆ in n -tetradecane is 0.008 at 298.15 K and 0.1 MPa (40); hence, the expected shift in the measured vapor pressure of the control sample is 0.8%. The solubility of SF₆ in the monoterpenoids is not known, so we assume that the magnitude of the effect is the same as for n -tetradecane. The Poynting correction to the pure-liquid fugacity is also small on the order of 1%. Any nonideality of saturated solute vapor is expected to be negligible because the pressures are low. Interaction of the solute vapor with the carrier gas could significantly change the measured vapor pressure (21), but the interaction virial coefficients are not known for these systems, so they are assumed to be negligible. Instead of trying to correct for these effects, we treat them all as uncertainties in the measurement. Hence, the quadrature sum of standard uncertainties associated with the method and instrument, the ideal gas approximation, and the sample purity is 8% for TPC and 7% for the other compounds, with expanded ($k = 2$) uncertainties of 16% for TPC and 14% for the other compounds.

Results and Discussion

The vapor pressures (p_{sat}) of five monoterpenoids (Scheme 1) and n -tetradecane were determined at temperatures of 283.15, 293.15, 303.15, and 313.15 K. Three simultaneous measurements of p_{sat} were made for each compound at each temperature, and the mean values are given in the tables and figures. The relative standard deviations of the replicate measurements ranged from 2% to 14%, and seemed not to depend on the temperature or the compound.

The gas saturation method does not require calibration; however, as discussed in the Experimental Section, there are some potential problems (e.g., leaks) that must be guarded against. The primary strategy for ensuring the quality of the data for the monoterpenoids was to make simultaneous measurements on a control compound, n -tetradecane. We chose n -tetradecane for a variety of reasons: its vapor pressure curve is well-known (41); in the temperature range studied, its vapor pressure curve is similar to those of the monoterpenoids; it is stable and unreactive; it is available commercially at low cost and with an acceptable purity. If the measured values of p_{sat} for n -tetradecane are the same as reference values, within the experimental uncertainty, that gives us confidence in the other values of p_{sat} that were measured simultaneously.

Reference values of p_{sat} for n -tetradecane were taken from the NIST ThermoData Engine (TDE) (42). The reference values are shown in Table 1 along with their estimated uncertainty. For comparison, the values of p_{sat} for n -tetradecane that were measured in the concatenated gas saturation apparatus also

TABLE 2. Vapor Pressures (p_{sat}) of the Monoterpenoids as a Function of Temperature (T)

T (K)	CAR ^a	HP ^a	IPC ^a	TM ^a	TPC ^b
	p_{sat} (Pa)				
283.15	2.61 ^c	0.727 ^d	0.737 ^d	0.457 ^c	5.64 ^c
293.15	7.16 ^c	2.17 ^d	2.52 ^d	1.41 ^c	14.5 ^c
303.15	15.6 ^c	5.25 ^d	7.37 ^d	3.72 ^c	32.3 ^c
313.15	26.0 ^c	12.7 ^c	19.5 ^d	9.06 ^c	72.7 ^c

^a The expanded ($k = 2$) uncertainty of these measurements is 14%. ^b The expanded ($k = 2$) uncertainty of these measurements is 16%. ^c This is the vapor pressure of the liquid phase. ^d This is the vapor pressure of the solid phase.

are given in Table 1. The difference between the TDE reference values and our measured values is less than the estimated expanded uncertainty of our measurements, Table 1. This is excellent evidence that the gas saturation apparatus is functioning properly.

It is interesting to note that the vapor pressures measured by gas saturation are all 5–11% higher than the reference values from TDE. Even though this is within the experimental uncertainty, it suggests the possibility of a small systematic error in the measurements. Although speculative, a non-negligible interaction between the solute vapor and the carrier gas could result in such an error (see the discussion of uncertainties in the Experimental Section). If this is the case, then it is also possible that the data for the terpenoids has a similar (small) systematic error.

The standard molar enthalpy of vaporization (ΔH_{vap}) or sublimation (ΔH_{sub}) at the mean temperature of the experimental range can be derived from the integrated form of the Clausius–Clapeyron equation. The reference data from Table 1 yield $\Delta H_{\text{vap}}(298.15 \text{ K}) = 71.4 \text{ kJ/mol}$. The gas saturation measurements from Table 1 yield $\Delta H_{\text{vap}}(298.15 \text{ K}) = 71.6 \text{ kJ/mol}$ (with a standard uncertainty of 1.3 kJ/mol), which is in excellent agreement with the reference value.

Table 2 shows the values of p_{sat} for the five monoterpenoids that were measured in the concatenated gas saturation apparatus. TM has the lowest values of p_{sat} in this temperature range, and they are very similar to the values for n -tetradecane. TPC has the highest values of p_{sat} , about an order of magnitude higher than for TM. This relatively small range of vapor pressures for the different compounds is advantageous in that it allows a single analytical procedure to be used for all of them. We are not aware of any previously reported vapor pressure measurements for these compounds in this temperature range, so no comparisons are possible. Nevertheless, we have confidence in the measurements because of the results for n -tetradecane.

Figure 2 shows Clausius–Clapeyron plots for IPC, TPC, CAR, and TM. IPC is a solid over the temperature range studied, and TPC, CAR, and TM are liquids. Linear regressions of the Clausius–Clapeyron plots yield $\Delta H_{\text{sub}}(298.15 \text{ K}) = 80.5 \text{ kJ/mol}$ (with a standard uncertainty of 1.1 kJ/mol) for IPC, $\Delta H_{\text{vap}}(298.15 \text{ K}) = 56.8 \text{ kJ/mol}$ (with a standard uncertainty of 2.8 kJ/mol) for CAR, $\Delta H_{\text{vap}}(298.15 \text{ K}) = 73.0 \text{ kJ/mol}$ (with a standard uncertainty of 2.4 kJ/mol) for TM, and $\Delta H_{\text{vap}}(298.15 \text{ K}) = 62.5 \text{ kJ/mol}$ (with a standard uncertainty of 1.0 kJ/mol) for TPC. HP melts in the temperature range studied, so we did not determine ΔH_{sub} or ΔH_{vap} for that compound.

The vapor pressure range measurable by the concatenated gas saturation method depends on a number of factors. Because the gas saturation method is generally used for low-volatility compounds, it is the low-pressure limit that is of most interest. In this work, with GC-FID as

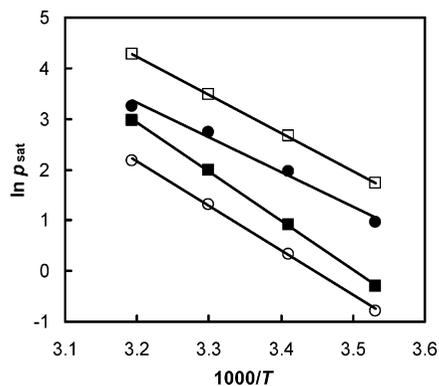


FIGURE 2. Clausius–Clapeyron plots for TPC (□), CAR (●), IPC (■), and TM (○).

the analytical method used to determine the mass of recovered vapor, the lowest vapor pressure measured was 0.4 Pa. However, we believe that it will be possible to measure vapor pressures that are orders of magnitude lower than that with our apparatus. One justification for this is that we have been working well above the detection limit of the GC-FID. By accepting smaller chromatographic peaks (and somewhat higher uncertainties), we could make measurements at lower pressures. We could also extend the pressure range by preparation of more concentrated analytical samples (e.g., by use of smaller eluent volumes or by solvent evaporation), and by an increase in the total volume of carrier gas (e.g., by an increase in flow rate of carrier gas and in the flow interval). And, of course, the analytical methodology could be optimized for low vapor pressures (e.g., larger injection volumes). In this way, we believe that it will be possible to measure vapor pressures for less volatile classes of compounds, such as carboxylic acids, that are also of interest for SOA formation.

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