Supporting Information

Exploring Matrix Effects on Photochemistry of Organic Aerosols

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Materials and Methods

Model SOM was prepared by dark ozonolysis of α-pinene (Alfa Aesar, 98%) in a 20 L flow tube; details can be found in Ref. (1). No seed particles were used. Particles exiting the flow tube were collected through a 1-m charcoal denuder with a Sioutas cascade impactor (2) using a single stage D (0.25 μm cut point at 9 SLM collection flow), which was modified in the UCI machine shop to accept a 25 mm CaF_2 window as the impaction substrate. The flow tube setup is able to generate several mg SOM per hour, resulting in typically ~10 mg of SOM collected after 2-3 hours of the flow tube operation. To prepare the 24-DNP/SOM film for the experiments, a 100 μL droplet of 0.01 M 24-DNP (Sigma-Aldrich, 99.9%, Pestanal analytical standard, with ~0.3 mL H_2O/g) in methanol (Fisher Scientific, Optima, HPLC grade) was added on the CaF_2 window containing a known mass of SOM (as determined by weighing the window before and after aerosol collection). The application of the droplet dissolved the SOM on the window, and the resulting slurry was allowed to sit for 30 min so that 24-DNP could permeate the SOM matrix and methanol could evaporate from the window. Different wait times were tried, and based on the stabilization of the 290 nm absorbance at wait times of 30 min and higher, it was assumed that the methanol had mostly evaporated. The resulting residue was sandwiched between two windows producing a thin, transparent, homogenous film. Although α-pinene SOM was reported to be solid-like in recent experiments (3), the presence of trace methanol and water and exposure to room air humidity which affects the viscosity (the film was exposed to ambient air at ~50% RH) allowed the film to slightly flow under pressure at room temperature. Furthermore, the SOM film likely retained residual water and methanol during the temperature-controlled experiments described below even though the photolysis compartment was purged with dry air to prevent water condensation on the outer surfaces of the windows. Photographs of the collected SOM and SOM loaded with 24-DNP are shown in Fig. S1 (a)-(c). A typical 24-DNP:SOM mass ratio in the film was ~1:50. This ratio was a compromise between two conflicting goals to have a small weight concentration of 24-DNP trapped inside SOM to ensure that it does not significantly affect the viscosity of the matrix, and at the same time have 24-DNP absorb more radiation than molecules in the surrounding SOM matrix do. Representative spectra of pure SOM and 24-DNP embedded in a SOM matrix are presented in Fig. S2, with a difference spectrum shown in the insert.
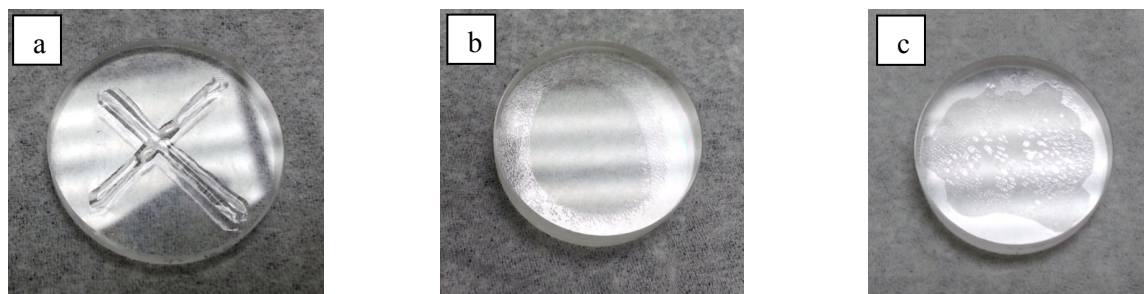
Figure S1. a) SOA material prepared in the flow reactor via α-pinene ozonolysis reaction and collected with a single-stage Sioutas impactor on a CaF$_2$ window. The cross resulted from rotating the impactor slit 90 degrees half-way though the collection. b) 24-DNP/SOM film prepared by evaporating a methanol solution of 24-DNP/SOM as described in the text c) "islands" forming in a reference SOM film after 4 hours of waiting at room temperature.
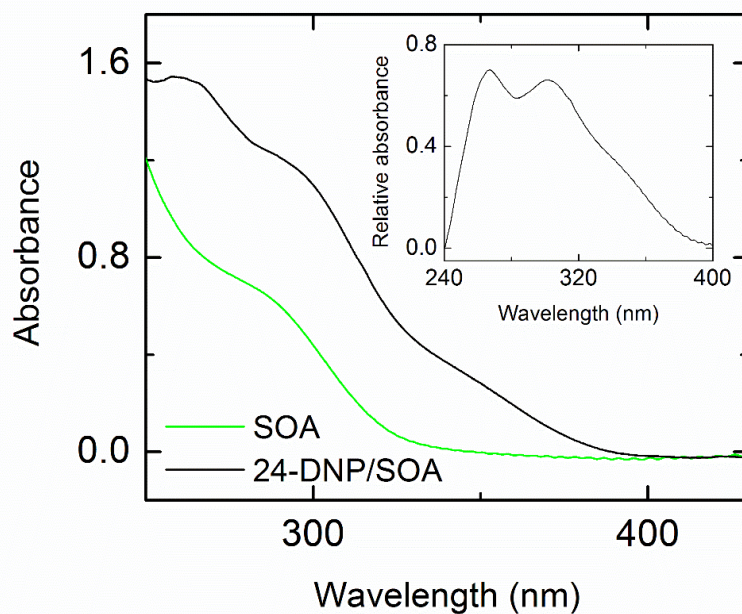

Figure S2. Absorption spectra of pure α-pinene SOM and 24-DNP embedded in α-pinene SOM matrix. The insert presents the difference spectrum, which has the characteristic absorption bands of 24-DNP.

To prepare 24-DNP/octanol samples, a 15 μL droplet of a 27 mM solution of 24-DNP in octanol (Sigma-Aldrich, 99%) was placed between the CaF$_2$ windows. The film thickness was estimated to be ~30μm based on the geometry of the liquid spot formed between the windows and the volume of the sample droplet. For aqueous experiments, 4.0×10^{-5} M aqueous solutions of 24-

DNP were prepared by dissolving 24-DNP in HPLC grade water and then acidifying with HCl to achieve a pH of ~1.4 to suppress ionization of 24-DNP.

The 24-DNP/SOM and 24-DNP/octanol samples were photolyzed in a setup designed for variable temperature film photochemistry experiments described in Ref. (4). A schematic picture of the setup is shown in Fig. S3. The windows containing sandwiched 24-DNP/SOM or 24-DNP/octanol were placed on a temperature controlled quartz microscope slide inside a compartment that could be purged with dry air in low temperature experiments to prevent water condensation. The windows were cooled to a desired temperature between -18 °C and 25 °C by combining a circulating water cooler connected to an aluminum heat sink and two Peltier coolers. The temperature of the samples was monitored with a type-K thermocouple mounted on the sample slide.
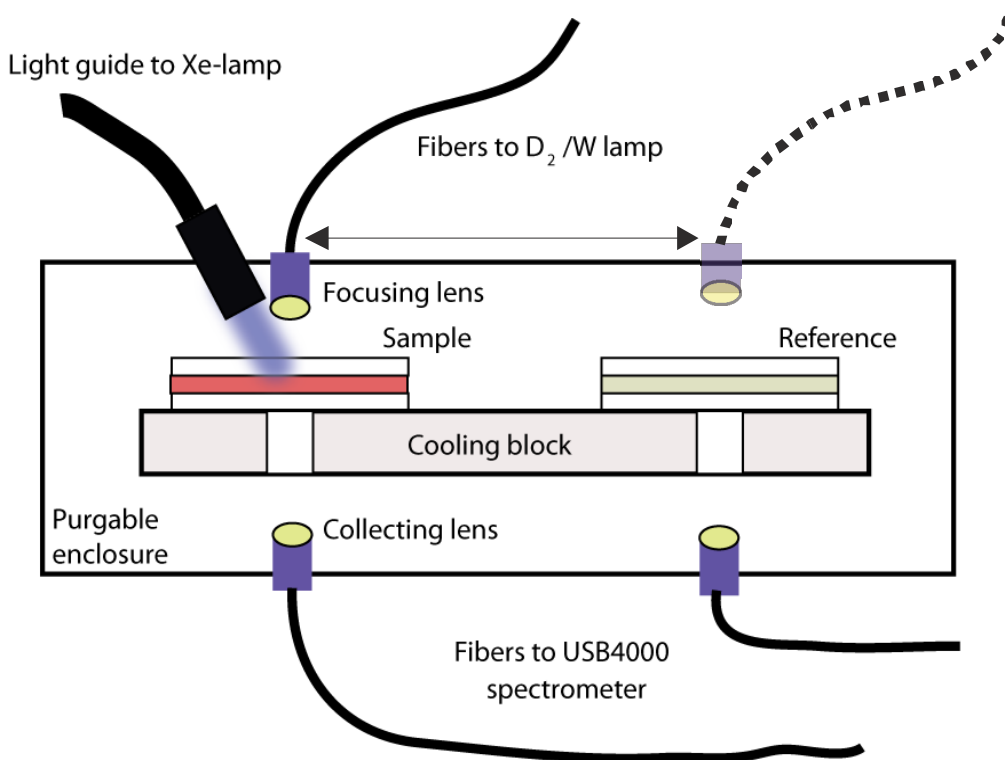
Figure S3. Experimental setup for temperature controlled SOM matrix photolysis. The fiber and collimating lens attached to the D_2/W lamp of the spectrometer can be shifted using a locking slider to measure transmission through either the sample (24-DNP/SOM or 24-DNP/octanol pressed between two windows) or reference (two blank windows or octanol pressed between two windows).

Two sets of experiments were carried around the freezing point of octanol; one where the 24-DNP/octanol film was just above its freezing point (-17 °C) and one where it had just frozen (-18 °C). The lowest temperature experiments were closely monitored and it was confirmed by visual observation as well as transmission that the frozen films stayed frozen during the whole experiment. The photolysis radiation was produced by a 150 W Xe arc lamp (Newport model 66902 lamp housing) and delivered to the film through a liquid light guide under a 15° angle with respect to the film normal. A 295 nm long-pass filter (Schott WG295) and a UV band-pass filter (Schott BG1) were used to achieve sufficiently powerful radiation while isolating a band (290-500 nm) of the actinic radiation of interest for tropospheric photochemistry. The photolysis was monitored by measuring the film transmission spectrum using a custom spectrometer consisting of a D_2/W light source, Ocean Optics USB4000 spectrometer, and 600 μm optical fibers to transmit the radiation between the spectrometer components (Fig. S3). Two methods for recording the reference spectra were used. In most of the experiments, the same pair of windows that was used for the photolysis experiment was used to acquire the reference spectrum at the sample position prior to the photolysis experiment at the desired temperature. The other possibility was to shift the optical spectrometer delivery fibers to a different position, where a pair of CaF_2 windows served as a reference for the SOM studies and 15 μL droplet of octanol between similar CaF_2 windows served as a reference for the experiments with 24-DNP/octanol films and for actinometry. Actinometry was performed under the same conditions using azoxybenzene actinometer in octanol/KOH film in similar manner as described in Ref. (5). The actinometer film was a 15 μL droplet of 63 mM azoxybenzene and 29 mM KOH in octanol. A representative spectrum of the actinometer film taken during photolysis is shown in Fig. S4.

One of the challenges faced during the 24-DNP/SOM photolysis experiments was the spontaneous physical changes taking place in the matrix material. After prolonged photolysis or dark storage times, the SOM film separated into "islands" (Fig. S1) and this effect was enhanced at elevated temperatures. The film break-up limited the timescales of the photolysis experiments, as it interfered with the measurements of the film transmission spectra significantly. The cause of the island formation is not clear, but the effect was not significantly affected when using quartz windows instead of CaF_2 windows, suggesting it is not due to any interaction with the window material. The organic material probably spreads during the experiment, and sample holders designed to prevent this should be used in future experiments.

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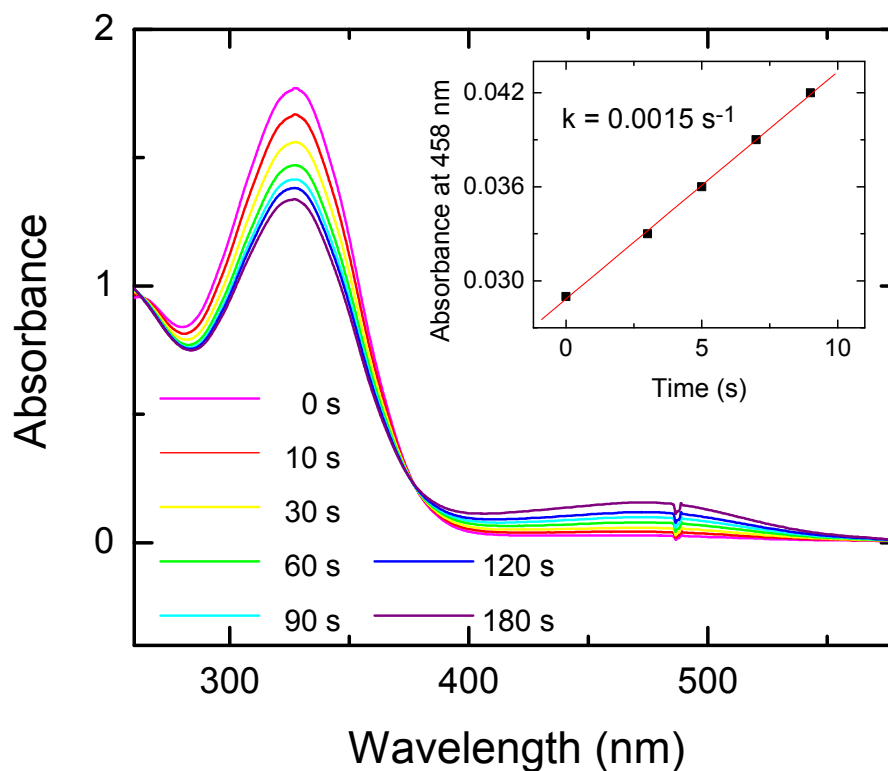
Figure S4. Azoxybenzene actinometer photolysis in octanol carried out under identical experimental conditions as the 24-DNP/SOM photolysis experiments. The insert shows the rate of increase of the 458 nm absorption of the azoxybenzene photoisomerization product. The photophysics and quantum yield of azoxybenzene are well known, and thus enable the quantification of the photolysis source, and the subsequent determination of the quantum yield of the studied photolysis process.

The apparatus used for photolysis of the aqueous solutions of 24-DNP consisted of a Shimadzu constant temperature cell holder inside a Shimadzu model 2450 UV−Vis spectrometer as described in Ref. (4). The cell holder was modified to hold a 9.5 mm liquid light guide illuminating a standard 10 mm quartz cuvette from the top by UV-radiation from the same photolysis source and filter combination as in the film experiments described above. The content of the cuvette was mixed with a micro stirrer (2-mag USA, MIX control eco, #MF90100). Absorption spectra of the solution were recorded periodically, with nanopure water in a matched quartz cuvette serving as a reference. For the actinometry experiments, an ethanol solution

consisting of 0.2 mM azoxybenzene/6.0 mM KOH was photolyzed under the same experimental conditions as the photolysis experiments.

Photolysis Experiments with Varying Relative Humidity

The experiments where relative humidity was changed at constant (room) temperature were performed in the same setup as described in the case of the temperature controlled experiments, and the SOM samples were prepared in a similar manner. In these experiments, however, the sample was not sandwiched between two windows. It remained on the surface of the Sioutas impactor collection window and was fully exposed to flowing air in the photolysis chamber in order to accelerate the 2,4-DNP/SOM drying/humidifying process (we verified in a separate set of experiments that the 2,4-DNP/SOM film did not appreciably evaporate from the window on the time scale of the photolysis experiments). The humidified air flowing over the sample was obtained by mixing a dry air flow and 100% RH air flow in a desired proportion. The relative humidity was recorded using a Vaisala HMP233 temperature and humidity probe. The 2,4-DNP/SOM film was exposed to the humidified/dried air for 12-24 hours before start of the photolysis to ensure that the slow water absorption equilibrium was reached. The results of these preliminary experiments are summarized in Fig. S5, where the photolysis rate constant of 2,4-DNP is plotted as a function of the relative humidity. (It should be noted that the lamp intensity was not the same as in the temperature-dependent experiments, so the rate constants shown in Fig. S5 are not the same as the room-temperature rate constants listed in Table 1 of the manuscript.) Although these experiments were more time consuming and harder to reproduce, a clear trend can be seen in the photolysis efficiency as the SOM viscosity changes with the relative humidity.
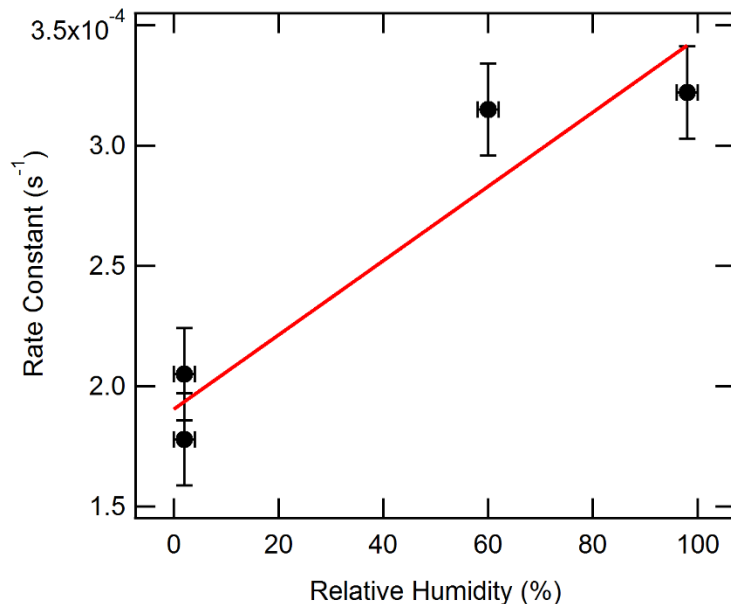
Figure S5. Change in the photolysis reaction coefficient k as a function of the relative humidity. The samples were exposed to the environmental conditions for 12-24 h prior to the photolysis. A clear enhancement in the photolysis efficiency due to decreased viscosity at higher RH is observed.

Photolysis of 24-DNP in Frozen Octanol

The frozen 24-DNP/octanol film produced a different kinetic behavior from the liquid 24-DNP/octanol film. A photograph of the frozen film and the time-dependent absorbance at 290 nm can be found in Fig. S6. The photolysis did not change the absorbance for the first 10-20 min of irradiation, but after that, the absorbance decayed at a rate that was faster than in all the other 24-DNP/octanol experiments. The resulting rate constant is included in Table 1 for completeness but not included in Fig. 2 in the manuscript. This implies a different mechanism in the frozen octanol film, possibly resulting from a phase separation into solid octanol and concentrated 24-DNP/octanol solution covering it, or from 24-DNP escaping as highly concentrated liquid droplets surrounding the frozen octanol crystals.

b)
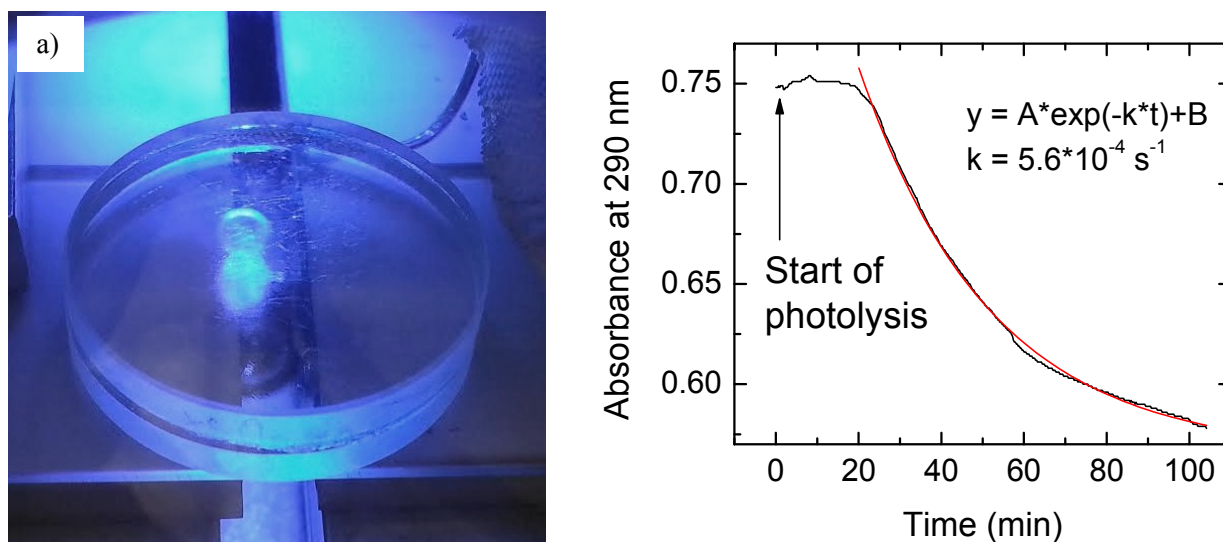
Figure S6. a) Photograph of the frozen 24-DNP/octanol film inside the photolysis apparatus; b) decay of the 290 nm peak as a function of time at T = -18 °C, where the film was frozen. The induction period preceding the exponential decay is reproducible (although the length of it varies).

Acid-Base Equilibrium for 24-DNP in SOM

It is important to point out that 24-DNP is a weak acid (pK_a = 4.1) and it ionizes in dilute and/or basic solutions. The ionization has a strong effect on the absorption spectrum (see Fig. S7), with the 24-DNP anion absorbing at considerably lower energies than the molecular form. As the SOM matrices are weakly acidic, and 24-DNP concentrations in the SOM films are high, it is predominately found in a molecular form (Fig. S7). The molecular form also dominates in the octanol films under the high concentration conditions used in these experiments. The aqueous photolysis experiments required a significantly lower concentration of 24-DNP, and in order to ensure that it remains in the molecular form, the solution was acidified to pH = ~1.4 using HCl. The molar extinction coefficient of 24-DNP is also known to change with the solvent (6), which was taken into account in the quantum yield calculations for 24-DNP/octanol and 24-DNP/water photolysis experiments. We measured the extinction coefficients of 24-DNP in different solvents (water, isopropanol, octanol), with the results shown in Fig. S8. Finally, we verified that the

molar extinction coefficient of 2,4-DNP does not significantly depend on temperature, as demonstrated in Fig. S9.
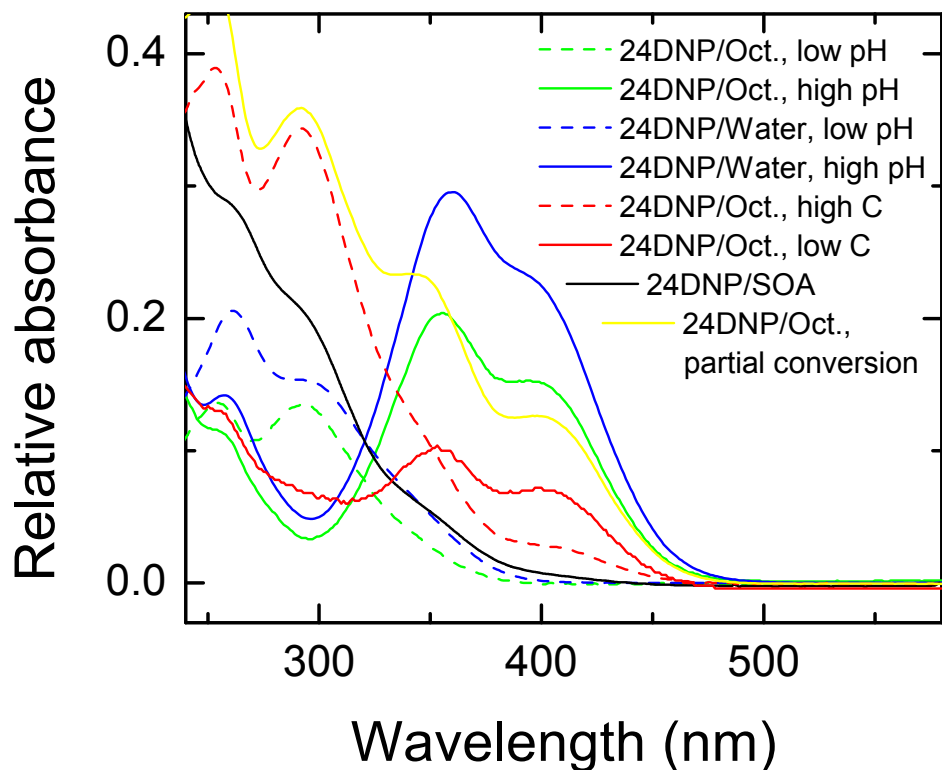
Figure S7. Comparison of the absorption spectra obtained at different concentrations and pH-values of 24-DNP solutions in octanol (Oct), water, and SOM. The solid line refers to lower concentrations and higher pH-values and the dashed lines refer to high concentrations and low pH-values. The absorbance at the y-axis is scaled to show the shapes of the spectra and the absorbance values are not the absolute values of the different conditions. At higher pH and/or lower concentrations, 24-DNP is ionized, leading to two characteristic peaks at 350 and 400 nm. At lower pH and/or higher concentrations (the condition applicable to the SOM matric) 24-DNP is not ionized, and the absorption shifts to the blue, with a characteristic peak at around 290 nm.
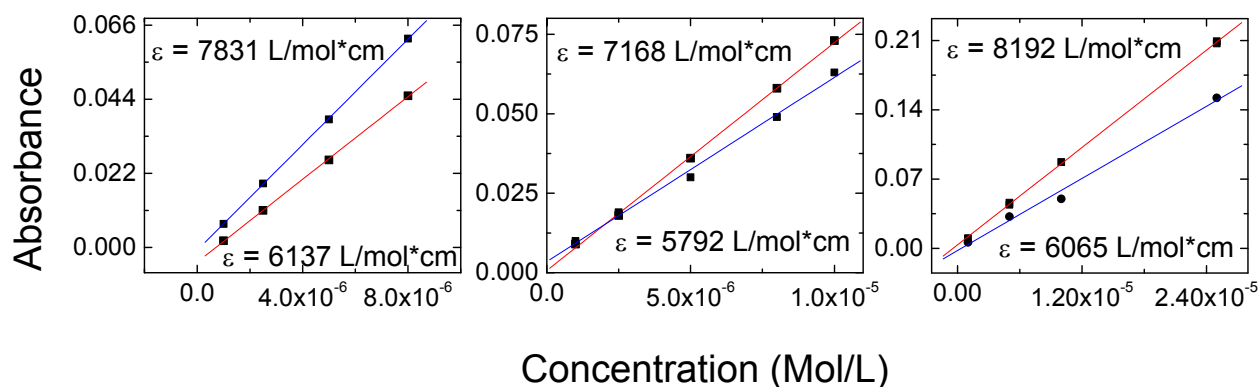
Figure S8. Molar extinction coefficients of 24-DNP in different solvents measured in this work. Beer-Lambert plots in a) water, b) octanol, and c) isopropanol. The absorbances were monitored in the molecular form (pH ~ 1) at 290 nm (blue) and in the ionic form (pH ~8) at 405 nm (red). The measurements were carried out at 20°C. The extinction coefficients were extracted from the linear fits of the Beer-Lambert plots.
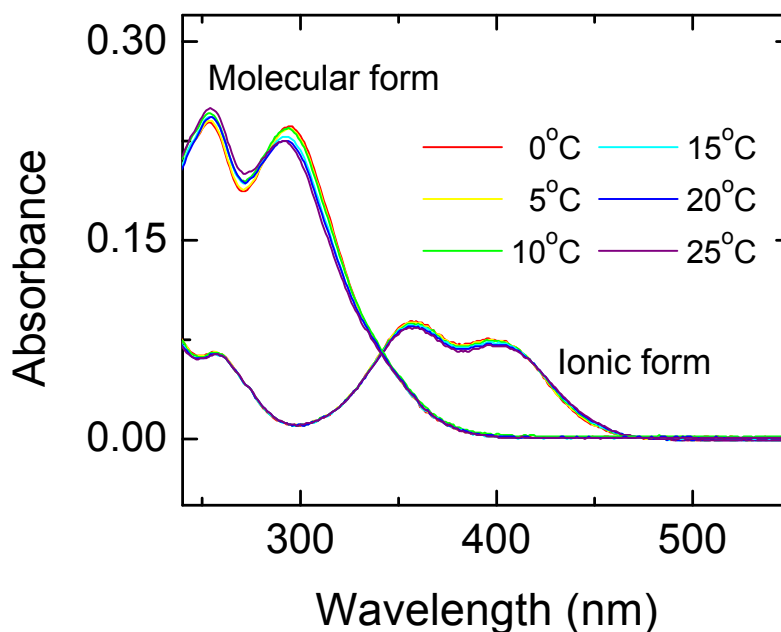
Figure S9. The UV-Vis absorption spectra of $4*10^{-5}$ M 24-DNP in octanol in its molecular form (pH ~ 1) and ionic form (pH ~ 8) at varying temperatures.

Temperature-Dependent Viscosity of Octanol and SOM

The temperature dependent viscosities of octanol were obtained from Ref. 7. The following approach was used to estimate the temperature dependence of SOM viscosity. The general glass transition viscosity was taken from Ref. 8, and paired with the average glass transition temperature of compounds found in α-pinene SOA (9). Room temperature viscosity of SOM was assumed to be 10^3 Pa·s, and the high temperature/low viscosity intercept was adapted from Ref. 8 by extrapolating data points to the maximum and minimum viscosity values including the aforementioned glass transition temperature and room temperature points. Finally the measurement temperature points were extracted from the extrapolation plot and fitted to the Arrhenius equation:

$$\ln \eta = \ln \eta_0 + \frac{E}{RT}$$

where η is the viscosity, E is the activation energy, R is the gas constant, and T is the temperature.

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