Supporting Information

Photochemical degradation of 4-nitrocatechol and 2,4-dinitrophenol in a sugar-glass secondary organic aerosol surrogate

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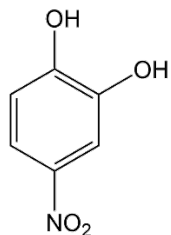Department of Chemistry, University of California, Irvine, Irvine, CA 92697

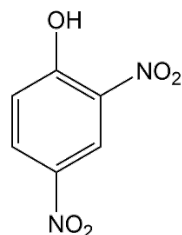## Contents

Summary: 15 pages, 12 figures, 1 table.

Chemicals Used in this Work

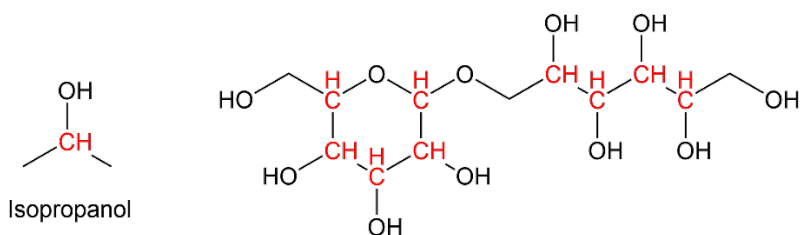## Photolysis subjects

4-nitrocatechol (4NC)   2,4-dinitrophenol (24DNP)

Matrices

Isopropanol

Isomalt

Figure S1. The chemicals used in this work. Photolysis was conducted on 4-nitrocatechol (4NC) and 2,4-dinitrophenol (24DNP). These molecules were photolyzed in three different solvents, namely water (not displayed), isopropanol, and isomalt (also known as isomaltitol). The structures of the materials used for the solvents have red highlights indicating the locations of the most easily-abstractable hydrogen atoms, due to the relative stability of the resulting carbon-centered radical products.

Additional Experimental Details

Photolysis

Experiments in the solid state were carried out using a custom apparatus (Fig. S2) described in previous publications.[1,2] The decay of 4NC in an UV-irradiated isomalt/4NC glass was monitored from the change in the UV/Vis absorption spectrum, recorded using an Ocean Optics DH-2000-DUV light source (the source has both D_2 and W lamps but only D_2 lamp was used), optical fibers and an Ocean Optics USB40000 spectrometer. Ocean Optics SpectraSuite was used to operate the spectrometer in "scope" mode. Measured intensities were averaged from 5 scans and the integration time was set in the range of 40-90 ms, depending on the thickness of the sample. Exported data was then averaged with a ~1 nm boxcar filter using MATLAB.
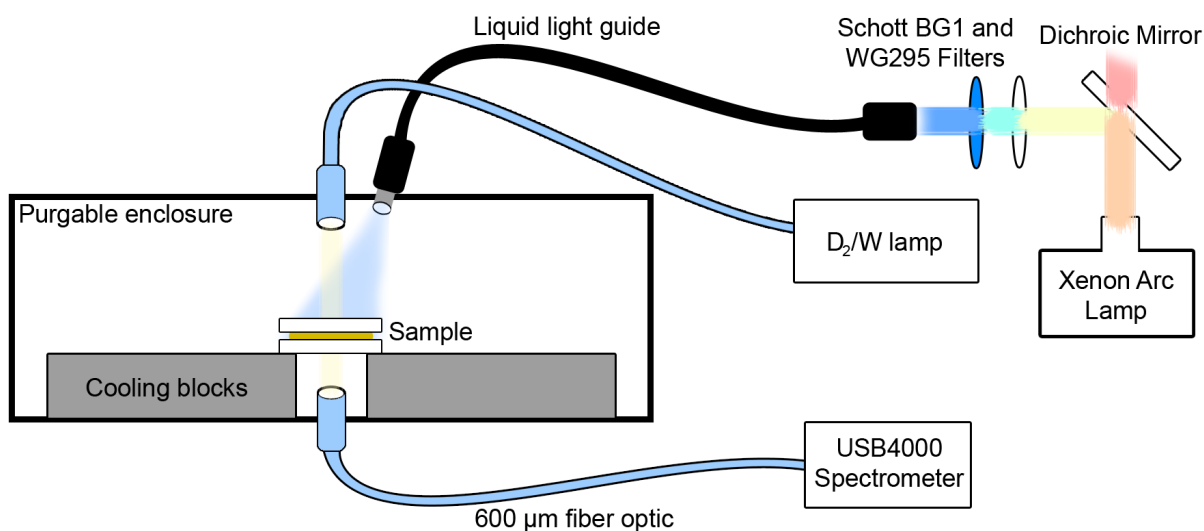

Figure S2. Apparatus used for solid state photolysis. The broadband probe radiation coming from the D_2/W source had a significantly smaller power output than the Xenon lamp used for photolysis and did not contribute to photolysis.

Photolysis was also conducted in octanol in order to validate previously reported results for 24DNP in Ref. 1. These samples were prepared by dispensing a 10 µL drop of either 20 mM 4NC or 24 mM 24DNP onto a SiO_2 window and gently laying another window on top. The resulting film between the windows had an estimated thickness of 25 µm. The solid state UV/Vis setup was used to analyze these samples.

Photolysis experiments in bulk solutions were carried out to compare to solid-state photolysis. These experiments were done directly inside a Shimadzu UV-2450 UV/Vis spectrophotometer operated with Shimadzu UV Probe 2.34 software as described in Ref. 2. 4NC was dissolved in water or isopropanol to get a concentration of 40 µM. The solution was placed in a standard 10 mm cuvette and remained inside the spectrophotometer for the duration of the experiment while being irradiated from above. A pure solvent was used as a reference.

For both solid-state and liquid phase experiments, photolysis was done by irradiating each sample with light from a 150 W Xe arc lamp (Newport 66902 lamp housing). The radiation reaching the sample was filtered by reflecting the output of the Xe lamp off a 280-400 nm dichroic mirror and directing it through a Schott WG295 long-pass filter and a Schott BG1 UV band-pass filter. The remaining radiation in the 290-450 nm range was directed through a liquid light guide (Edmunds #53-691) onto the solid sample at a 15 degree angle (Fig. S2). The use of the liquid light guide reduced the filtered lamp power by 75% but permitted easy switching between solid and liquid state setups. The photon flux density of the light exiting the light guide and reaching the sample can be found in Fig. S3.
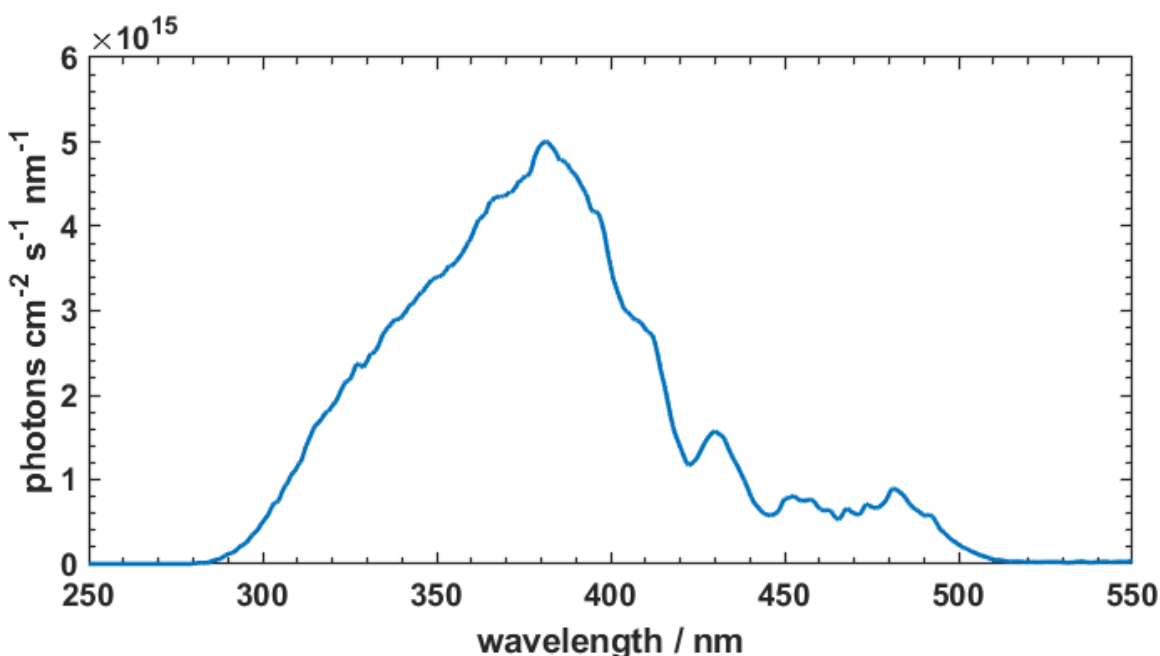

Figure S3. Photon flux density $F(\lambda)$ (photons cm^{-2} s^{-1} nm^{-1}) of the Xenon arc lamp used for photolysis. Spectrum was calculated from the spectral irradiance measured with by a StellarNet BLACK-Comet spectrometer. The measurement was taken after the light guide, with the same setup used for photolysis.

Product Analysis

Following photolysis, the sandwiched windows were placed in a beaker with around 15 mL of deionized water to cover the top of the stack. The windows were kept in the water for up to a couple of hours to allow the isomalt to fully dissolve. The resulting solution was light-yellow in color. Once the windows were removed, the sample solutions were placed in a rotary evaporator and the volume was reduced to about 1 mL. Samples were then transferred into 300 μL glass vials. Product analysis was conducted with a Thermo Scientific Vanquish Horizon ultra performance liquid chromatograph (UPLC) in line with a Vanquish

Horizon photodiode array (PDA) spectrometer and a Q Exactive Plus high resolution mass spectrometer (HRMS). A heated electrospray ionization (HESI) source was used to generate ions for HRMS and was used solely in negative ion mode. The HESI capillary temperature was set to 300°C and a spray voltage of 2.5 kV. The scan range was 50-750 *m/z* units. The PDA was set to measure absorbance between 190-682 nm.

HRMS data was processed using the Thermo Scientific software Freestyle 1.6. For each run, a sample was collected and analyzed before and after photolysis, allowing for detection of photolysis products. Each photolysis sample analyzed in the UPLC/HRMS had a "photolysis blank" which was the remaining 4NC/glass mixture after sample preparation. Virtually no other peaks were observed other than 4NC in these non-photolyzed glass samples, suggesting thermal degradation was not a major issue. Molecular formula assignments by Freestyle were confirmed with the MIDAS Formula Calculator version 1.2.3 (https://nationalmaglab.org/user-facilities/icr/icr-software) and were within 2 ppm mass tolerance. Since Freestyle places no restrictions on the number of C, H, N, or O atoms, the advantage of the Formula Calculator was that it helped enforce the correct valence rules and avoid unphysical formulas. All other elements were excluded from formula assignments since neither 4NC nor its solvent contained them.

Additional Experimental Observations Worthy of Reporting

Some noticeable formation of bubbles was sometimes noticed when retrieving samples after photolysis. Other times this bubbling required the sample to be heated back up first, as melting the glass sample was occasionally done for clean-up if the sample was not being retained for UPLC-PDA-HRMS analysis. It is possible that these bubbles could be gaseous photoproducts that are lost when redissolving the samples after photolysis. We are noting this as a curious observation, worthy of further investigation.

Measurements of Molar Extinction Coefficients

Molar Absorptivity Measurements

The molar absorptivity of 4NC has been reported in aqueous solution at various pH values.[3] Though the absorption spectrum of 4NC in solid isomalt had a similar shape to the spectrum in an acidic aqueous solution, experiments were conducted to determine the molar absorptivity, ε, of 4NC in isomalt. Since the path length of the sample could be easily measured using digital calipers, the absorbances of 4NC in isomalt of a fixed concentration were measured at various sample thicknesses (b). Equation S1 was used to determine ε from measured absorbance, $A(b)$, for a fixed concentration $C = 2.07$ mM (Fig. S4).

$$A(b) = \varepsilon \cdot b \cdot C \qquad\qquad \text{Equation S1}$$

The molar absorptivity at the peak of the 350 nm absorption band was found to be $(7.5 \pm 0.6) \times 10^3$ M^{-1} cm^{-1}, which is comparable to the previous reported value of ~6800 M^{-1} cm^{-1} at 347 nm for 4NC in a pH = 2.0 aqueous solution.[3] A comparison to an acidified solution is relevant since the acid suppresses ionization of 4NC anion, which has a different absorption spectrum.

The wavelength-dependent molar extinction coefficients are shown in Figure S4. These spectra were produced by dividing the measured absorbance spectra by the concentration and path length of their respective samples. For 4NC in isomalt, the molar extinction coefficients were calculated from an average of five samples of varying thicknesses. Shading represents a 95% confidence interval from these samples. The low values for 4NC in isomalt below 250 nm are likely due to instrumental limitations in UV transmission in the solid UV/Vis setup. The molar extinction spectrum shown for 4NC in isopropanol was produced from an absorption spectrum of a 172 µM solution. We note that absorption spectra of 4NC in isopropanol at much lower concentrations had a visible secondary peak at 430 nm as a result of partial ionization of 4NC (for example, Fig. S6). The shape of the absorption spectra are similar but the spectrum in isomalt displays a bathochromic shift of the order of 5 nm from 345 nm in liquid isopropanol to 350 nm in solid isomalt.
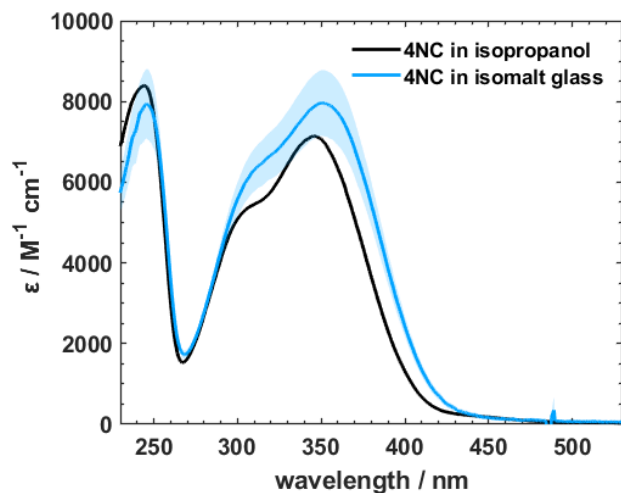
Figure S4. Molar extinction coefficient as a function of wavelength for 4-nitrocatechol in (black) isopropanol and (blue) isomalt glass. Shading around the isomalt trace represents a 95% confidence interval from five measurements.
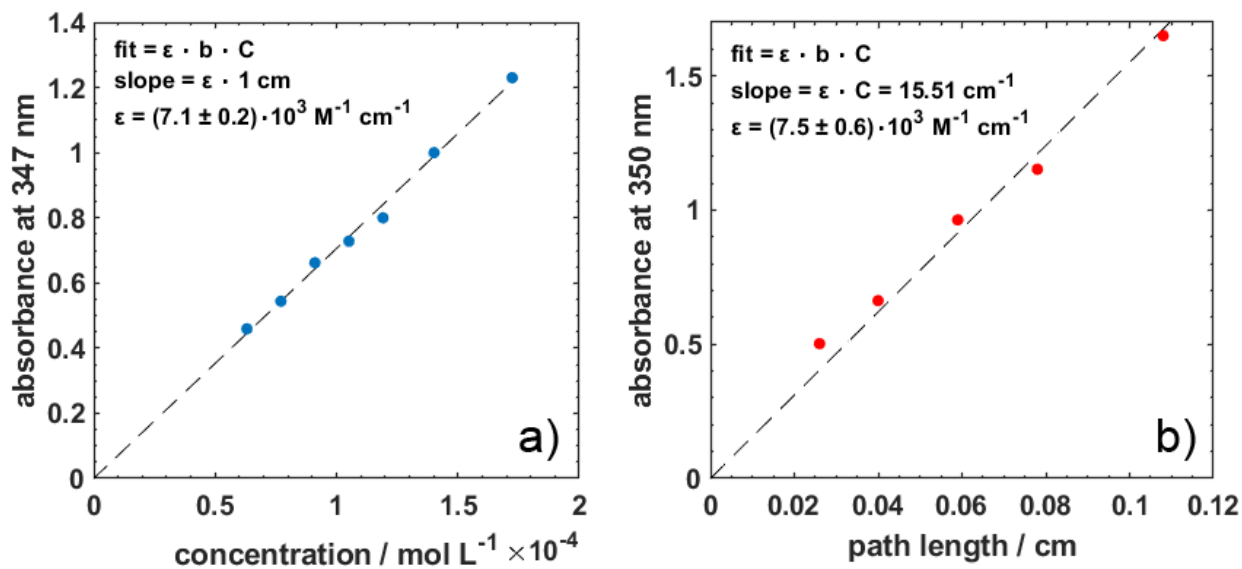

Figure S5. Beer's law plots for 4NC in (a) isopropanol solution and (b) isomalt glass at the peak of the absorption spectrum (347 nm for 4NC in isopropanol and 350 nm for 4NC in solid isomalt). The concentration was fixed in the isomalt experiments at 2.07 mM and each data point corresponds to a new preparation of glass. The intercept for both fits was fixed to the origin.

Results from Photolysis in Aqueous Solution

As a check to see if the reaction truly progressed through a hydrogen abstraction mechanism, a control was done to compare between solvents with respect to the number of easily-abstractable hydrogen atoms. The hydrogen atoms in water should be significantly more difficult for 4NC* to abstract than those in these organic molecules. Isopropanol and isomalt were both added to water such that the concentration of easily-abstractable hydrogen atoms (one in isopropanol and nine in isomalt, Fig. S1) was the same in both solutions. The chosen concentrations were 13 M for isopropanol and 0.58 M molar for isomalt in water. The photolysis of 4NC occurred at a linear decay rate of $(1.8 \pm 0.2) \times 10^{-6}$ s^{-1} in the aqueous isopropanol solution and $(6.1 \pm 0.8) \times 10^{-6}$ s^{-1} in the aqueous isomalt solution. 4NC may have reacted quicker in the isomalt solution due to the existence of more reactive parts of isomalt than accounted for. The reactions between 4NC and the organic molecules were slowed significantly in these water-containing solutions as compared to the pure organic solvent, confirming that reaction with the organic solvent is the preferred reaction pathway for 4NC*.
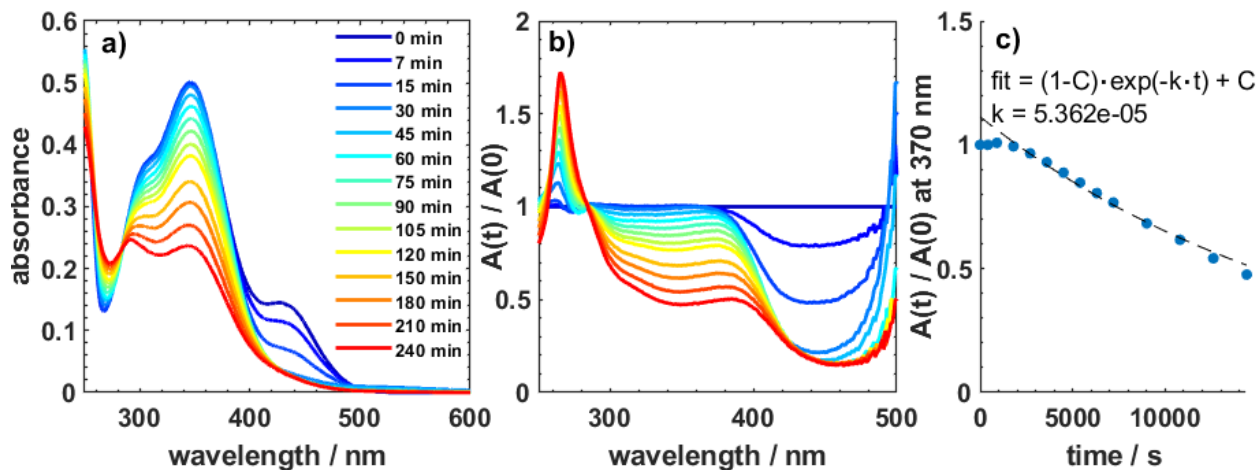
Results from Photolysis in Isopropanol Solution

Figure S6. Absorption spectra recorded during photolysis of a 40 mM solution of 4NC in isopropanol (a), absorption spectra from (a) normalized to the absorbance at t=0 (b), and the decay in normalized absorbance at 370 nm with an exponential fit (c). The fit in (c) was done relative to the 30 min mark when the absorbance first started to decrease. We note that in this example 4NC solution in isopropanol is not acidified, and some ionization of 4NC occurs producing the 4NC anion band at 420 nm. The anion's band disappears faster, and we start our fit in (c) after this band is gone. We have not explored the effect of acid-base equilibrium on photolysis in this work as the focus was on photolysis in isomalt, where such anion formation did not occur.
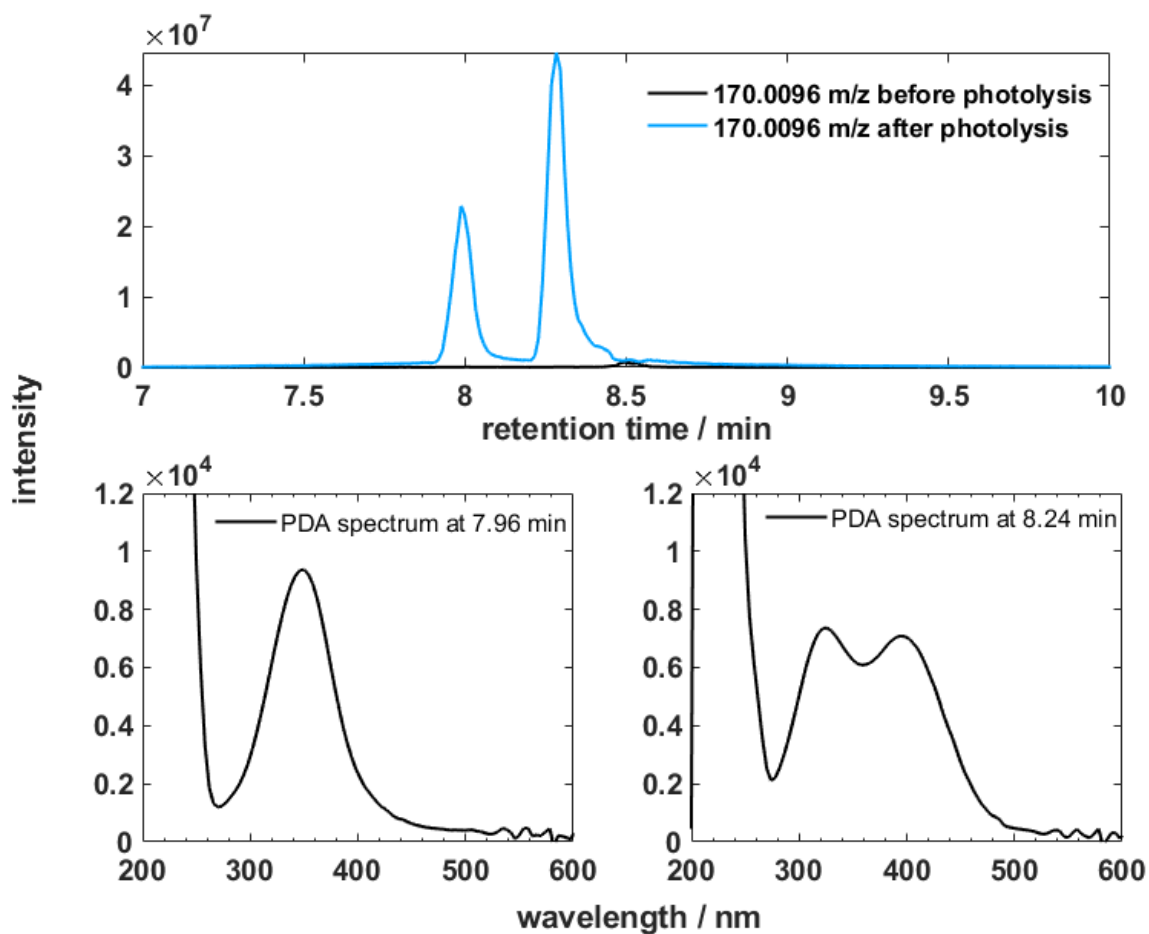
Figure S7. Selected ion chromatogram for the *m/z* 170.0096 photolysis products (top) of 4NC in isopropanol and associated UV/Vis PDA spectra with the product retention times (bottom). The product eluted around 7.96 min has a distinct peak at 330 nm. The product around 8.24 min has a broad absorption band with a peaks at 325 nm and 400 nm.

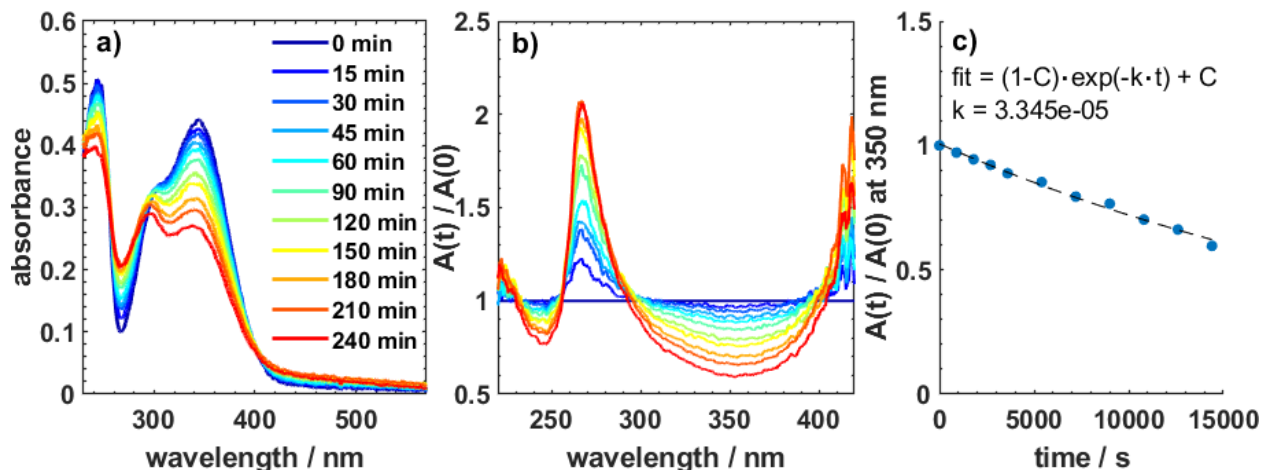# Results from Photolysis in Octanol Films

Figure S8. Plot of the absorption spectra of 21 mM 4NC in octanol film obtained at different times during photolysis (a), the same absorbance spectra normalized to the absorbance at t = 0 (b), and the decay in normalized absorbance at 350 nm (c). Strong growth in absorbance was observed between 250-300 nm, as well as above 400 nm. Low absorbance values at 400+ nm cause noise in the normalized absorbance (an artifact of normalization that can be disregarded).
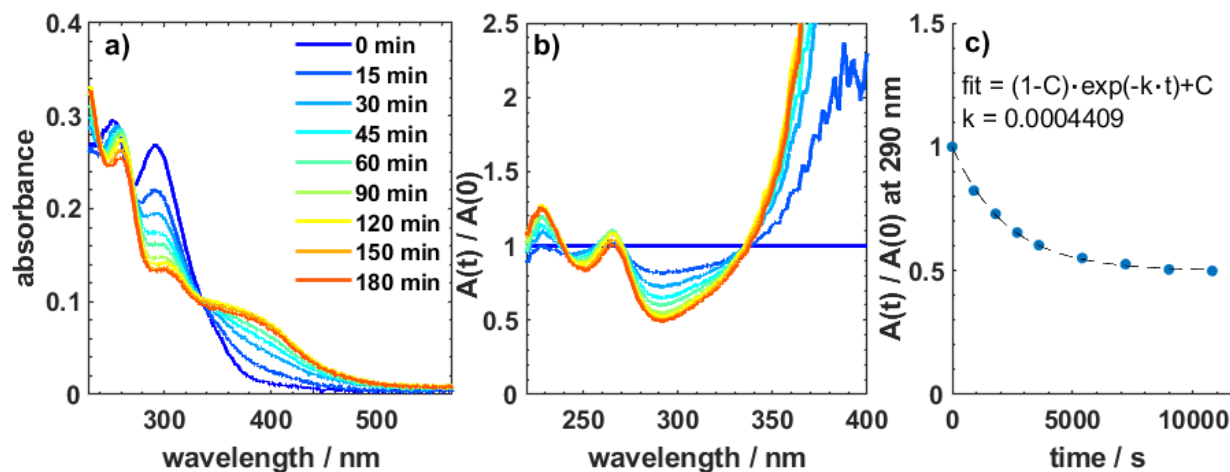

Figure S9. Plot of the absorption spectra of 24 mM 24DNP in an octanol film obtained at different times during photolysis (a), the same absorbance spectra normalized to the absorbance at t = 0 (b), and the decay in normalized absorbance at 290 nm (c). The shapes of these spectra are similar to those observed in 24DNP/octanol photolysis in Ref. 1.
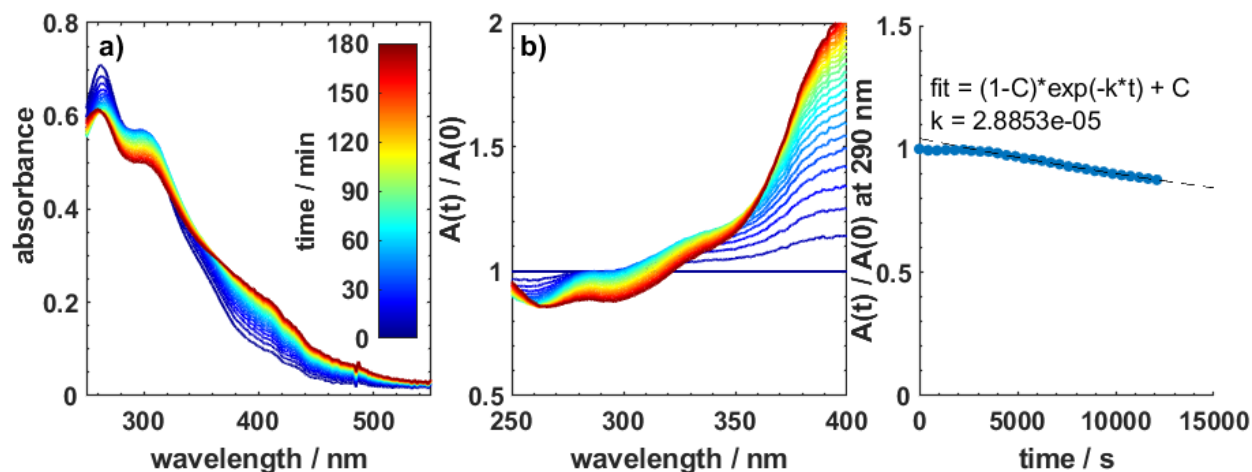
Results from Photolysis in Isomalt Glass

Figure S10. Plot of the absorption spectra of 24DNP in isomalt glass obtained at different times during photolysis (a), the same absorbance spectra normalized to the absorbance at t = 0 (b), and the decay in normalized absorbance at 290 nm (c). Measurements were taken every 7.5 minutes due to expectations of quick reactivity based on findings in octanol. The fit in (c) was applied only after 30 minutes into photolysis due to a lack of decay during that time.

Table S1. Rate constants and quantum yields from photolysis of 4-Nitrocatechol in isomalt glass

	k (s^{-1})^a / 10^{-5}	$k(1-\beta)$ (s^{-1})^b / 10^{-5}	$\langle \phi \rangle^c$ / 10^{-5}
Trial 1	1 ± 7^d	1.5 ± 0.1	-
Trial 2	1 ± 4	1.2 ± 0.1	2 ± 8
Trial 3	5 ± 3	1.4 ± 0.2	8 ± 5

[a]The rate constant k is derived from the exponential decay in Equation 1 (main text). [b]The value of the slope from a linear fit that corresponds to the product $k(1 - \beta)$ from Equation 2 (main text). [c]Effective quantum yield, calculated with k from Equation 1, averaged over a 100 nm interval surrounding 350 nm. [d]Effective quantum yield is not reported due for Trial 1 to relatively large uncertainties in the rate constant.
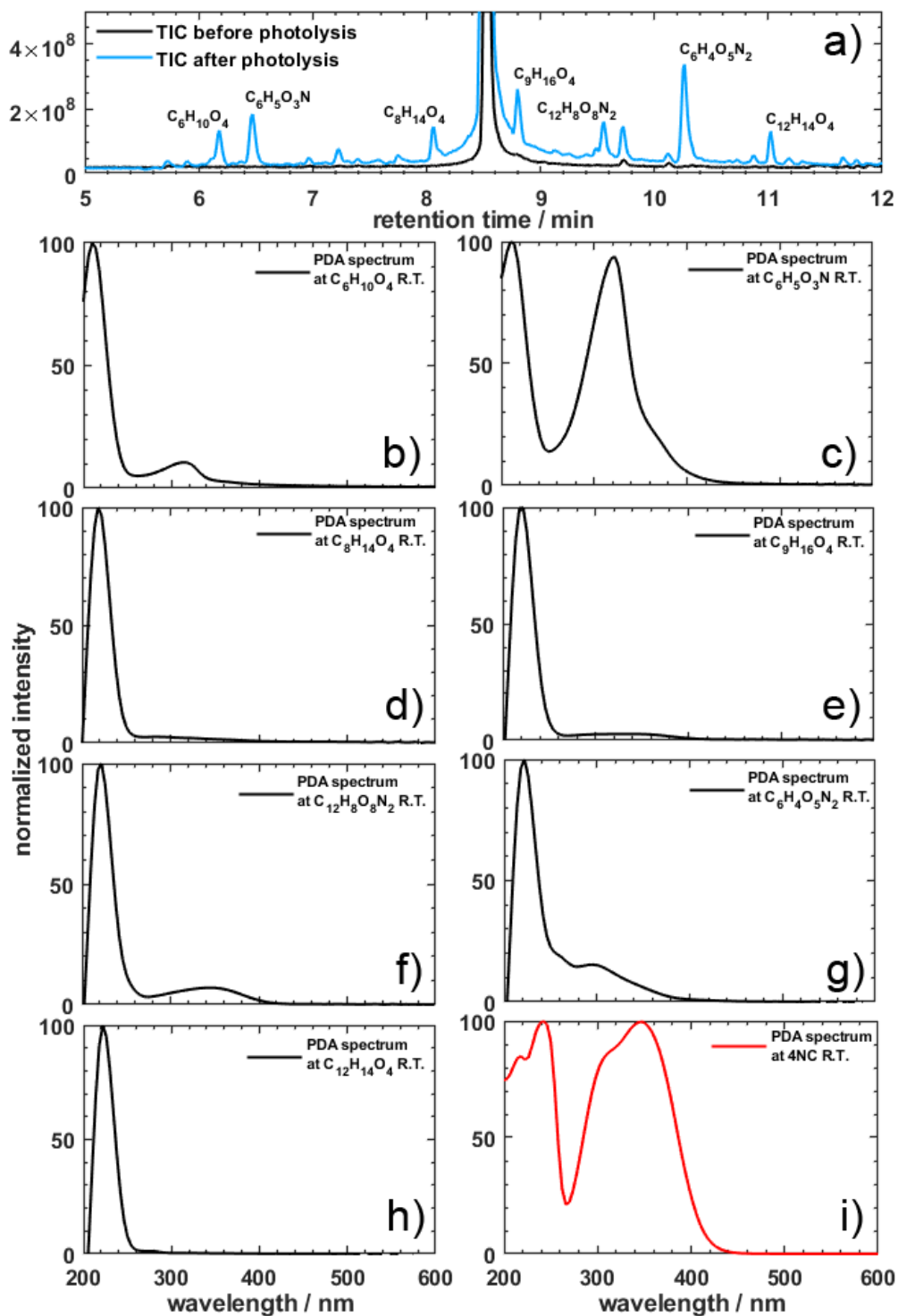
Figure S11. UV/Vis PDA spectra of products formed from photolysis of 4NC in isomalt glass. Each PDA spectrum was recorded approximately 0.07 min before the MS retention time. Formula assignments are calculated from the largest *m/z* value at each peak retention time.
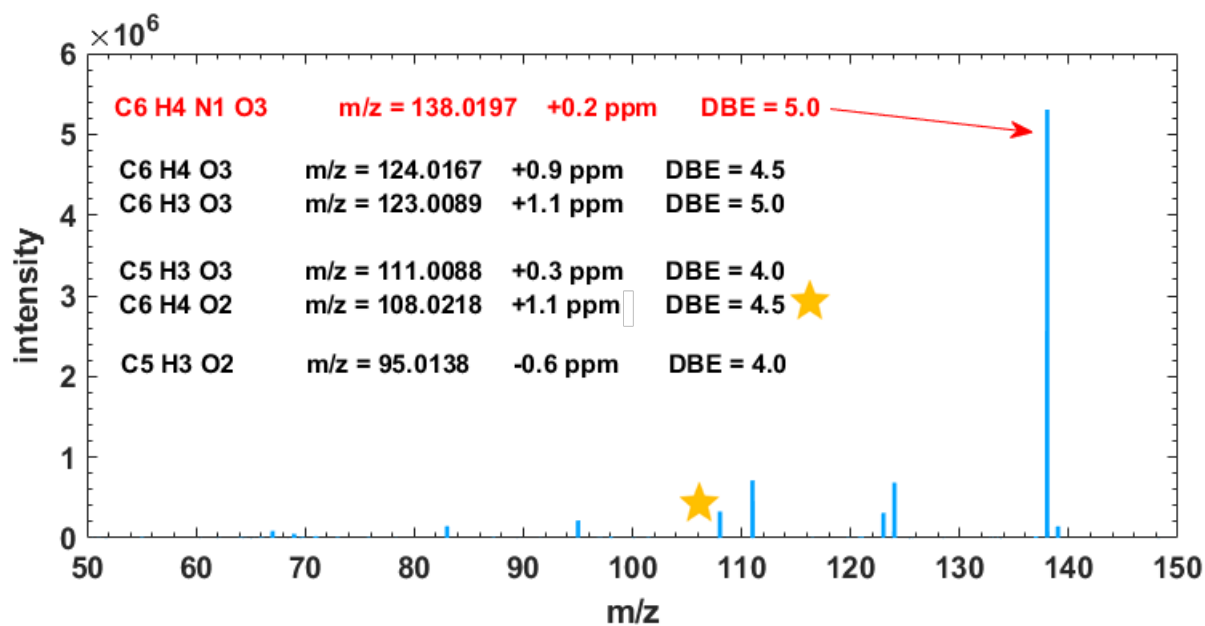
Figure S12. MS/MS spectrum for *m/z* = 138.02 with outputs from the molecular calculator overlayed for the major peaks in the mass spectrum. The parent ion corresponds to $C_6H_4NO_3^-$, which could be either nitrophenol or 4-nitrosocatechol. The peak labeled with a gold star corresponds to loss of NO from the parent, suggesting the 4-nitrosocatechol structure. A peak corresponding to the loss of NO_2 would be at *m/z* 92, but it was not observed. More complex fragmentation processes are also taking place corresponding to the loss of N, NH, HCN, and HCNO.

References

(1) Lignell, H.; Hinks, M. L.; Nizkorodov, S. A. Exploring Matrix Effects on Photochemistry of Organic Aerosols. *PNAS* **2014**, *111* (38), 13780–13785.

(2) Epstein, S. A.; Shemesh, D.; Tran, V. T.; Nizkorodov, S. A.; Gerber, R. B. Absorption Spectra and Photolysis of Methyl Peroxide in Liquid and Frozen Water. *J. Phys. Chem. A* **2012**, *116* (24), 6068–6077.

(3) Nothnagel, E. A.; Zitter, R. N. The PH Dependence of the Ultraviolet and Visible Absorption and the Resonance Raman Spectra of 4-Nitro-1,2-Benzenediol in Aqueous Solution. *J. Phys. Chem.* **1976**, *80* (7), 722–727.