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Photochemistry of Nitro-Polycyclic Aromatic Hydrocarbons

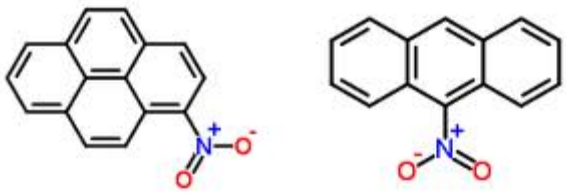
August 9, 2011

Photochemistry focuses on the absorption of light by atoms and molecules leading to chemical reactions. With the absorption of light, pure substances' electrons jump from their ground states to their excited states, where chemical reactions and the formation of new chemical species commence.

In my research, I focused on two specific nitro polycyclic aromatic hydrocarbon compounds (nitroPAHs): 9-nitroanthracene and 1-nitropyrene (**Scheme 1**). These nitroPAHs form from incomplete combustion reactions and nitration reactions in the atmosphere. During experimentation, both are excited using a Xenon lamp to mimic sunlight and are dissolved in different solvents that mimic the micro-environment in which each compound may be found in the environment.

The first goal of my research was to corroborate that the Beer-Lambert equation (1) holds for the nitroPAHs that I studied. This equation proposes that the extinction coefficients (ε) are wavelength (λ) dependent and are a characteristic physical property of molecule. This equation further implies that the concentration (c) of a molecule in a solution is directly proportional to the absorbance (A) at a given wavelength. The absorbance of the molecule is measured in a cell that has a predefined optical path length (b).

$$A = \varepsilon_{\lambda} bc \qquad (1)$$



Scheme 1. Molecular structures of 1-nitropyrene (left) and 9-nitroanthracene (right). Both are composed of nitrogen, hydrogen, oxygen and carbon atoms.

A second goal of my research was to investigate if dissolution of these nitroPAHs in different solvents affects the magniture of their extiction coefficients and, thus, their absorption properties. Finally, a third goal was to investigate if light absorption by these nitroPAHs results in deradation of these compounds and if there was any dependence on the solvend used.

INSTRUMENTATION

The high performance liquid chromatography (HPLC) is used to separate a mixture of different molecules in a solution so chemists can analyze, characterize, and purify each of the individual molecules in that mixture. The HPLC is shown in **Figure 1**. The Xenon lamp was used to simulate the sunlight and induce photo-degradation and is shown in **Figure 2**. The setup consists of a lamp, filter, electronic-controlled shutter, sample holder and stirrer. The UV/Vis spectrometer measures the probability of light absorption by molecules in a particular region of the electromagnetic spectrum, which allows chemists to characterize and to obtain information about the physical properties of a given molecule in different solvents. It is shown in **Figure 3**.

Figure 1

Figure 2

Figure 3

BEER-LAMBERT LAW (BLL)

BLL EXPERIMENTATION

MATERIALS:

- Methanol (or Acetone)
- Ethanol
- Acetonitrile
- Cyclohexane
- 9-Nitroanthracene
- 1-Nitropyrene
- Beaker (140mL)
- Scale (g)
- 20 mL Brown bottle
- Spatula
- Cuvette

- Several Pipets (with one 1000P vol. pipet)
- Vol. Flask (25 mL)
- Spectrometer

PROCEDURES:

1. Obtain materials; rinse equipment (NOT solutes or solvents) thoroughly with methanol and let dry.

2. Once dry, record mass of vol. flask and zero the scale. Use a spatula to add a small amount of 9-Nitroanthracene (approx. 0.0032g) into the vol. flask. Record mass in notebook.

3. **WHEN MAKING SOLUTIONS, DO THE PROCEDURE UNDER AN AIR HOOD:** Fill vol. flask completely with Ethanol; an unused pipet will need to be used to make the surface tension of the solution pass the flask line. Use a vol. flask top to cover the flask and shake the solution until the 9NA is completely dissolved. Once dissolved, pour as much solution as possible into a 20 mL brown bottle; close with lid and dump the rest of the solution in a waste beaker.

4. Taking the beaker, fill the container with as much ethanol (WITHOUT the mixture of 9NA) that will be needed to complete the experiment (the amount poured will depend on the data table).

5. Create a data table showing the solution with different concentrations of 9NA in ethanol (shown below). **DO NOT** forget to make a column for your baseline.

6. Use a 1000P vol. pipet with TWO tips, (ONE tip used for the solvent and ONE tip used for the solute) and follow the data table made to mix one measurement of 9NA in ethanol in the 20 mL brown bottle with one measurement of the ethanol in the beaker. Pour both measurements within a cuvette. Shake briefly and put the cuvette cap on. Close any unused solutions with a lid.

7. Walk over to the spectrometer and place cuvette within the machine; press start and record absorbance from 200 nm to 500 nm. Set time to be 1 min. Begin the spectrum.

8. **RINSE CUVETTE WITH ETHANOL AND LET DRY AFTER EACH SCAN (used a CLEAN pipet to do so).** Afterwards, repeat steps 7 and 8 until all measurements from the data table have been recorded on the spectrometer. Once done, rinse all equipment with methanol.

9. Repeat steps 1-9 for acetonitrile and cyclohexane in 9NA. **Make sure all equipment have been rinsed very thoroughly and left alone to dry.** Then, experimentation using 1NP can be done. Repeat steps 1-9 to do so.

BEER-LAMERT DATA TABLE

SOLUTION #	VOL. 9NA (mL)	VOL. SOLVENT (mL)	CONC.(M)
1	3.75	0.00	VARIES
2	3.25	0.50	VARIES
3	2.75	1.00	VARIES
4	2.25	1.50	VARIES
5	1.75	2.00	VARIES
6	1.25	2.50	VARIES
7	0.75	3.	VARIES
8	0.25	3.50	VARIES
9	0.00	3.75	0.00

BEER-LAMBERT RESULTS

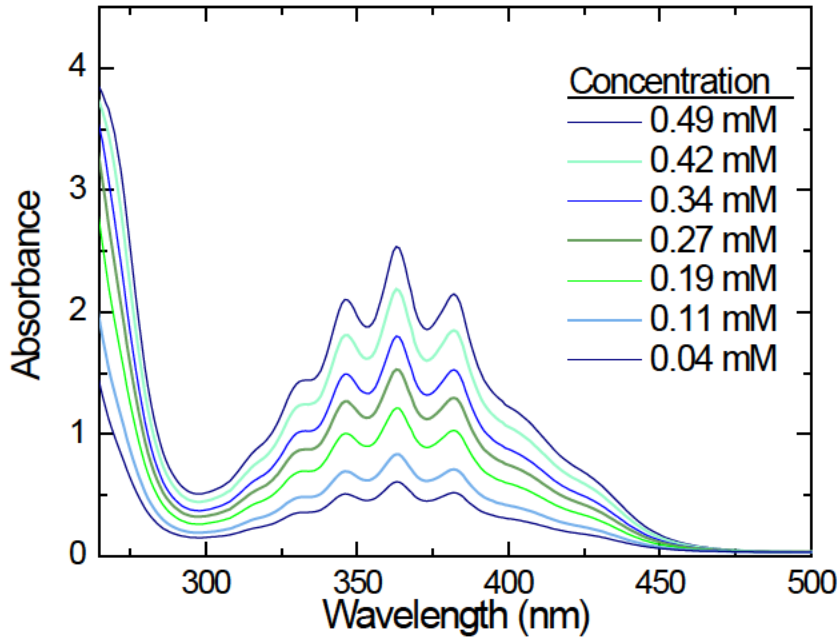


Figure 4: Demonstrates how a decrease in concentration of the solute (9NA) within an ethanol solvent results in a proportional reduction of absorptivity.

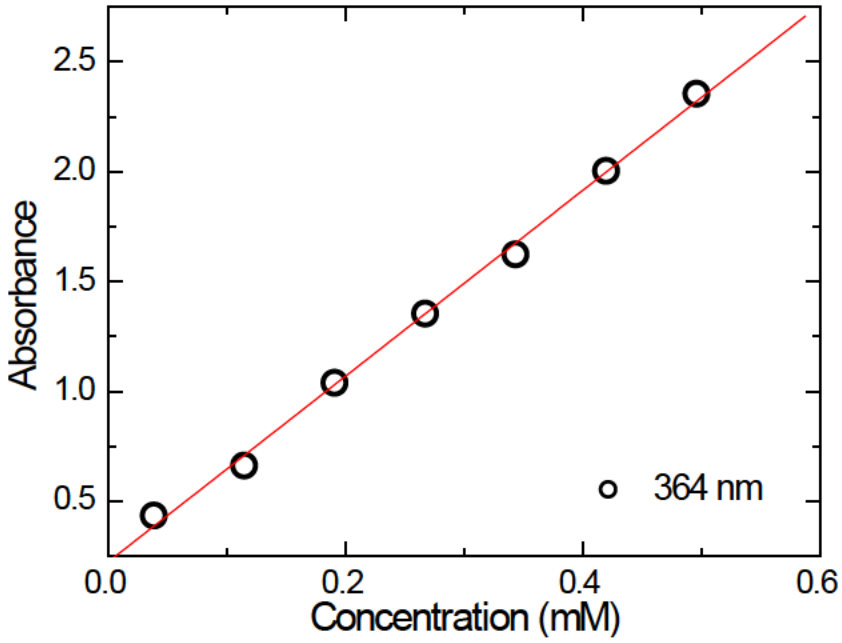


Figure 5: Enforces the Beer-Lambert Law by showing how the concentration is directly proportional to the absorbance

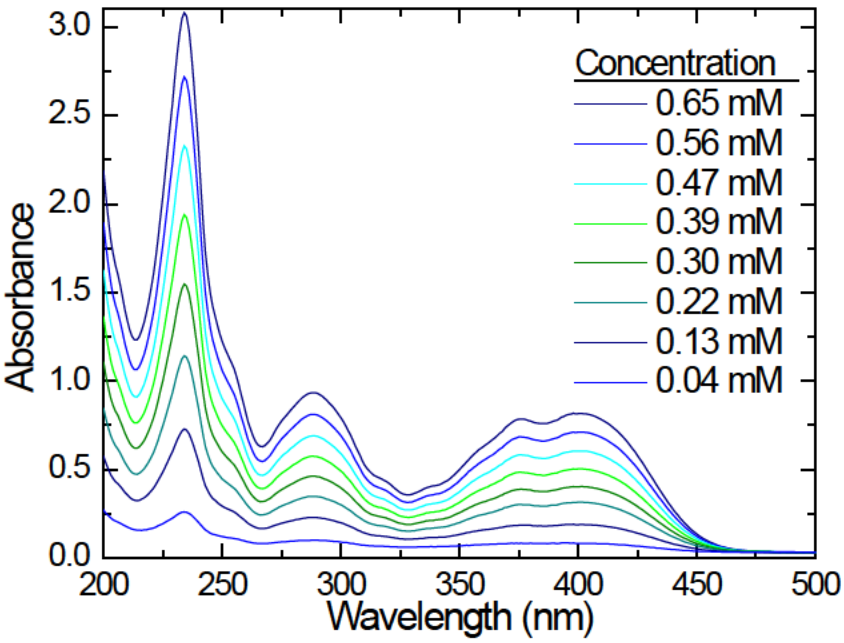


Figure 6: At various concentrations, the absorption spectrum of 1NP is shown within acetonitrile.

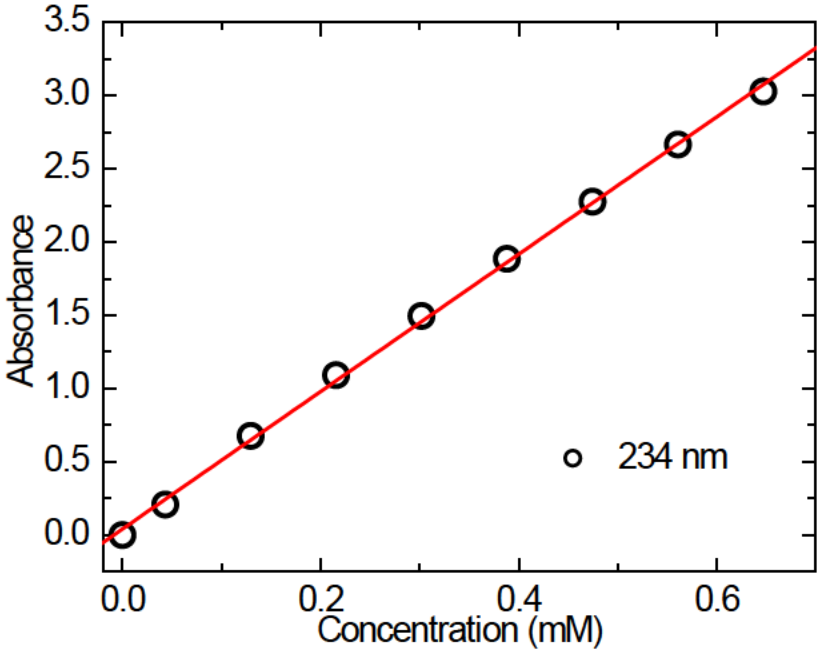


Figure 7: The absorbance vs. the concentration proves to show a linear trend.

Epsilon Dependency upon Wavelength and Solvent

Solvents	9NA ε (382 nm)	9NA ε (363 nm)	1NP ε (234 nm)	1NP ε (363 nm)

	/ M-1cm-1	/ M-1cm-1	/ M-1cm-1	/ M-1cm-1
Cyclohexane	630 ± 20	710 ± 30	1880 ± 50	520 ± 20
Acetonitrile	420 ± 10	500 ± 10	4690 ± 60	960 ± 10
Ethanol	360 ± 10	420 ± 10	3500 ± 80	740 ± 20

This table shows how the extinction coefficient (ε) is dependent upon the wavelength and the solvent. The epsilon for Cyclohexane in 382 nm defers from the epsilon for Ethanol. Two wavelengths were chosen for each solute (9NA and 1NP) to show this dependency upon wavelength within the same solvent. For example: the epsilon for 382 nm and 363 nm in Acetonitrile defers for both, even though the same concentration of 1NP was used in the experiment.

PHOTODEGRADATION

HPLC EXPERIMENTATION

MATERIALS:

- Methanol (or acetone)
- 9-Nitroanthracene
- 1-Nitropyrene
- Ethanol
- Acetonitrile
- Cyclohexane
- Spectrometer
- Spatula
- HPLC
- Blunt syringe (100 mL)
- Several pipets (with one 1000P vol. pipet)
- Xenon Lamp (with stir bar)
- Box (blocks light)
- Brown bottle (20 mL)

PROCEDURES:

1. Obtain materials; rinse equipment (NOT solutes or solvents) thoroughly with methanol and let dry.
2. **WHEN MAKING SOLUTIONS, DO THE PROCEDURE UNDER AN AIR HOOD:** Once dry, take an unused pipet to fill the cuvette with acetonitrile (3/4 full is fine) and put the cap on the cuvette.
3. Go to the spectrometer and place the cuvette within the machine; press start and record absorbance from 200 nm to 500 nm. Set time to be 1min. Begin the spectrum. This will be the baseline.
4. Using a spatula, add a very small amount of 9NA into the cuvette; shake, put the cap on and take the spectrum of this solution. **IF** the absorbance is ~1.5, move onto the next step; **IF NOT**, use a pipet to add droplets of acetonitrile until the absorbance is ~1.5 (this is assuming too much 9NA was added in the beginning of step 4; add more 9NA if the situation applies). Save final spectrum.

5. **Turn off lights and use red light for better results.** Otherwise, quickly pour the solution into a beaker and place into box. Rinse the cuvette and let dry.

6. Afterwards, use the 1000P vol. pipet to measure 1.75 mL of the solution from the beaker into the clean and dry cuvette. Measure 2.00 mL of acetonitrile into the cuvette as well. Place cuvette into the box.

7. Go to the spectrometer and scan the absorbance of the solution within the cuvette.

8. Under an air hood, use a blunt 100 mL syringe to take a 100 mL sample of the solution from the cuvette. Going to the HPLC, insert the sample into the machine and scan for 10-15 min. **Rinse syringe with methanol before each scan.**

9. Place solution within the box and go the Xenon Lamp. Irradiate the solution within the cuvette for 30 sec with stir bar.

10. Repeat steps 7 and 8 until complete (or close to) decay of 9NA. Record and save all data on the computers. Data tables will be represented using graphs.

11. Repeat steps 1-10 for acetonitrile and cyclohexane in 9NA. **Make sure all equipment have been rinsed very thoroughly and left alone to dry.** Then, experimentation using 1NP can be done. Repeat steps 1-11 to do so.

HPLC RESULTS

By using the high performance liquid chromatography I was able to analyze each, individual molecule that played a part in the degradation of 9NA in the solutions of ethanol and acetonitrile. I prepared a calibration curve (not shown) for the HPLC which allowed me to calculate the change in concentration of the 9NA with irradiation time. The peak at a retention time of 4.3 min corresponds to the 9NA, shown in **Figure 8**.

Figures 9 to 12 show the results of the photo-degradation experiments. For instance, in **Figure 10**, there is a decrease of absorbance above 345 nm because below this wavelength, photoproducts absorb the light more strongly as time progresses and the 9NA degrades. With degradation, the photoproducts begin to absorb the light more often than the 9NA.

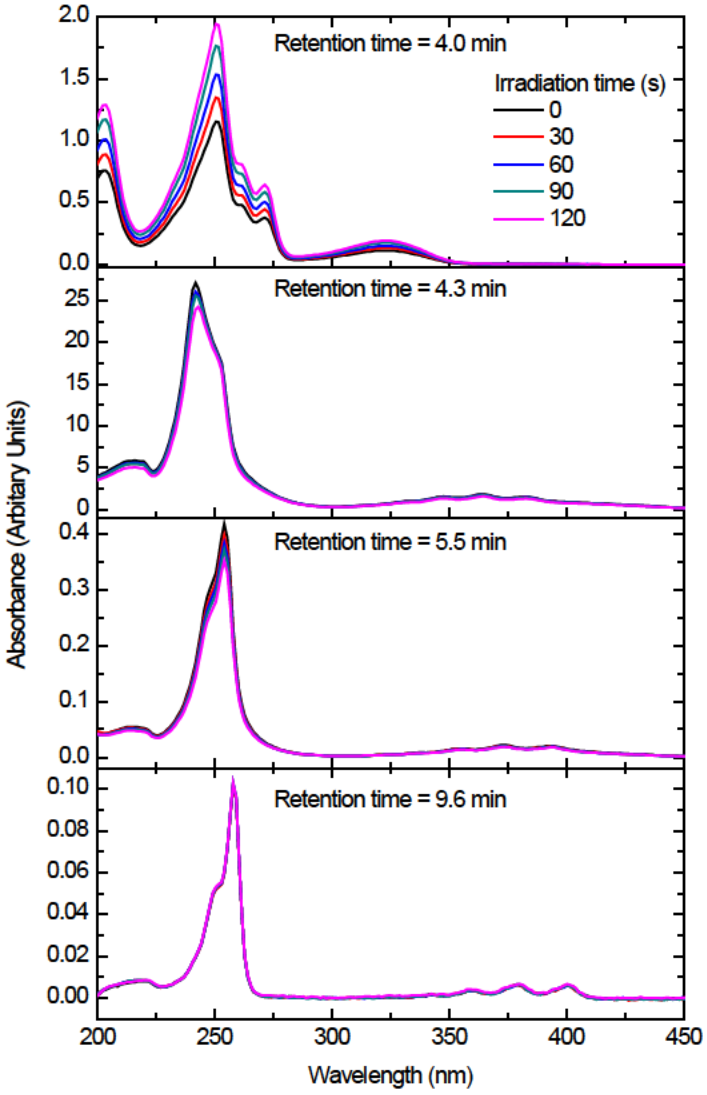


Figure 8: The HPLC was used to separate the reaction mixture and for observing the absorption spectra of the 9NA and its photoproducts following irradiation with a Xe lamp.

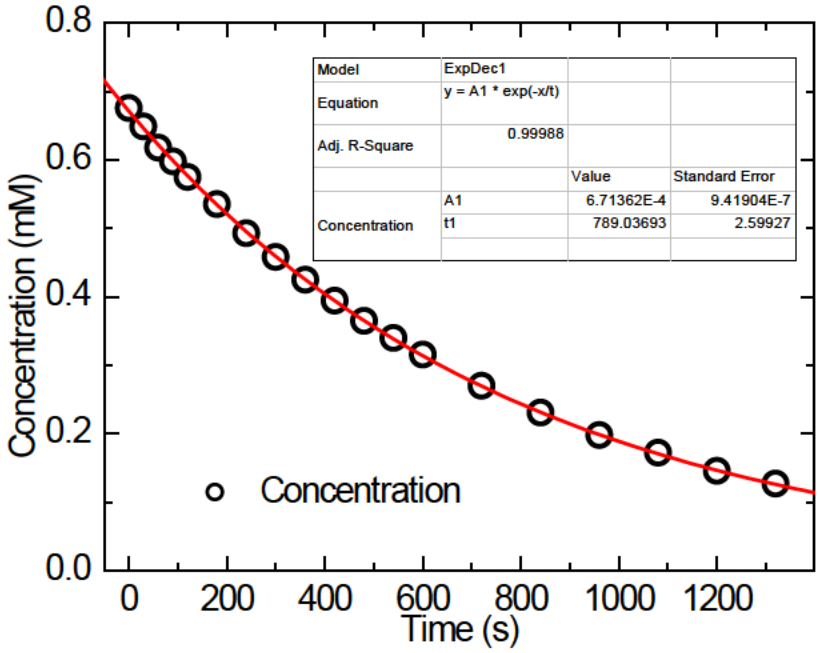


Figure 9: As time increases and more photo-products are being formed, the concentration of 9NA decreases.

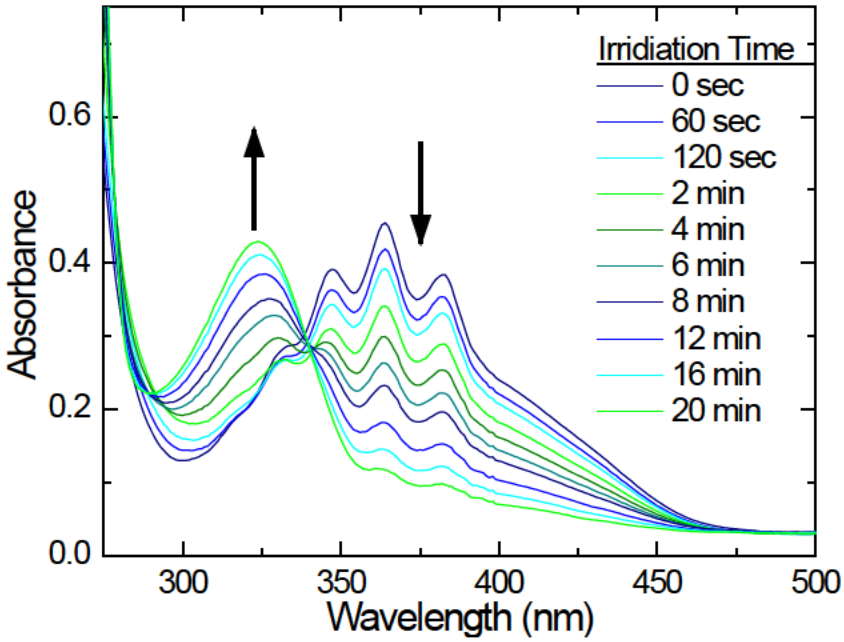


Figure 10: This is the irradiation of a solution of 9NA in acetonitrile.

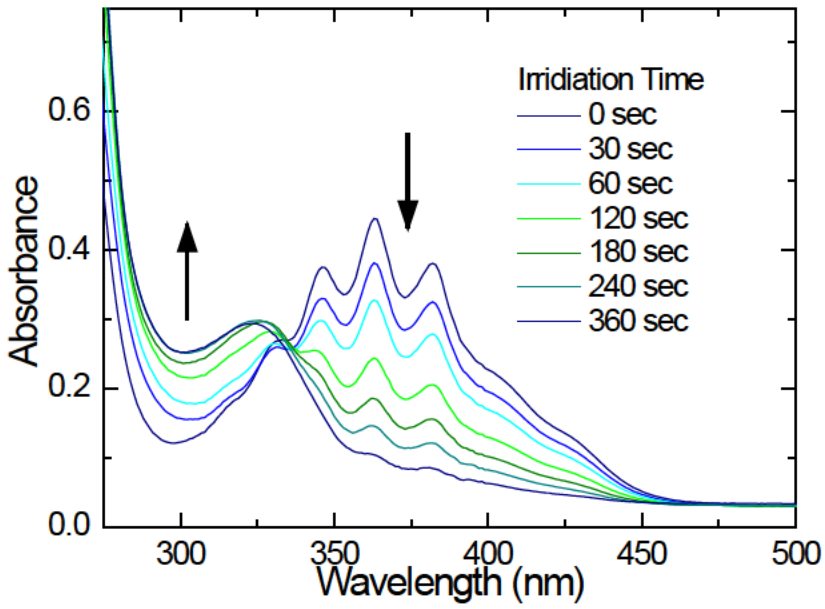


Figure 11: Irradiation of a solution of 9NA in ethanol. As the 9NA degrades, the results are shown to be similar to those seen in Figure 8.

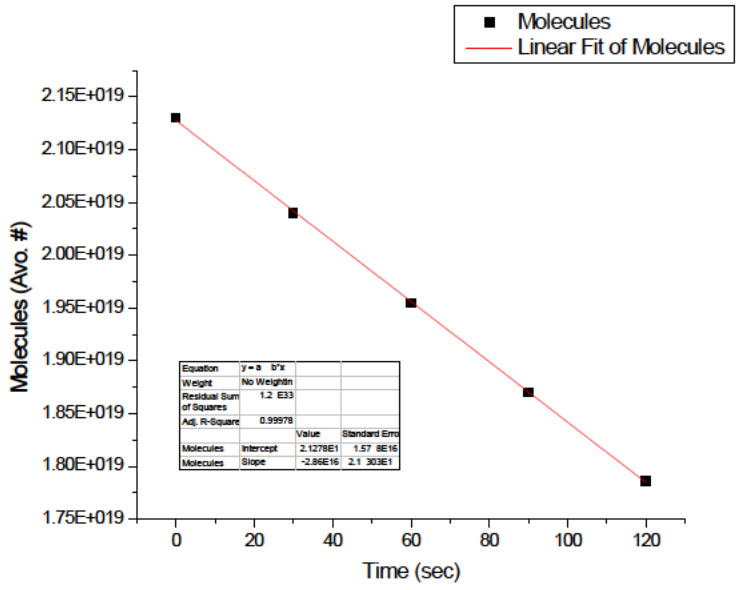


Figure 12: This graph shows the decrease of 9NA molecules over time; i.e. the more irradiation from the Xe lamp, the less 9NA molecules within each trial.

CONCLUSIONS

Through a series of experiments, the Beer-Lambert Law has been proven and enforced by showing how the concentration of each solution are directly proportional to the absorbance. The molar extinction coefficients of 9-nitroanthracene and 1-nitropyrene have been proven to be both wavelength (λ) and solvent dependent. However, I was able to show that the efficiency of 9-nitroanthracene's degradation is solvent dependent. More research needs to be done to quantify and prove the effect that solvents have on the degradation process, as well as how irradiation affects a solution of 1-nitropyrene. Visible light does in fact degrade these two compounds, which would explain why both are transformed into new compounds after they absorb sunlight in the environment. Whether or not these new compounds formed after degradation is harmful to society has yet to be proven through additional experimentations.

Nonetheless, with 9-Nitroanthracene it has been shown that as time increases with the irradiation of the xenon lamp, more photoproducts are being formed and the concentration of 9-nitroanthracene decreases. In other words, through a series of tests and calculations, it is shown that 9NA decreases as time progresses and the photoproduct yield increases because of this light-induced chemical change. This decrease results in a reduction in the 9NA-molarity in the solution over time, which implies a decrease in the number of moles of 9NA in the solution and therefore, decreases the amount of 9NA molecules in the experiment.

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