Shining a Light on Foodborne Carcinogens: The Photochemistry of 2-Amino-1-methyl-6-phenylimidazo[4,5-b]pyridine

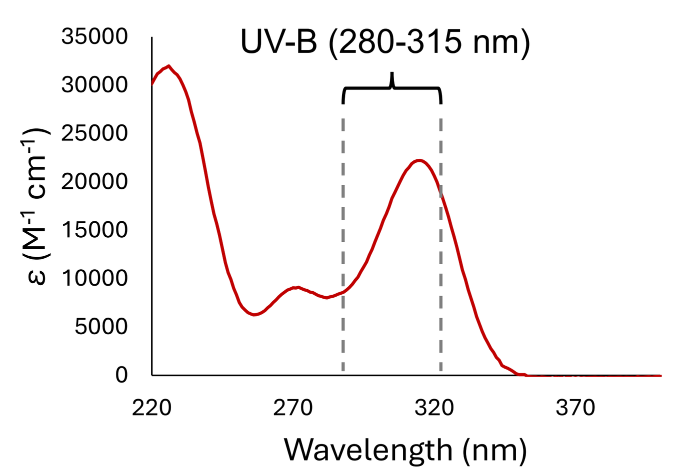
THE COLLEGE OF WOOSTER

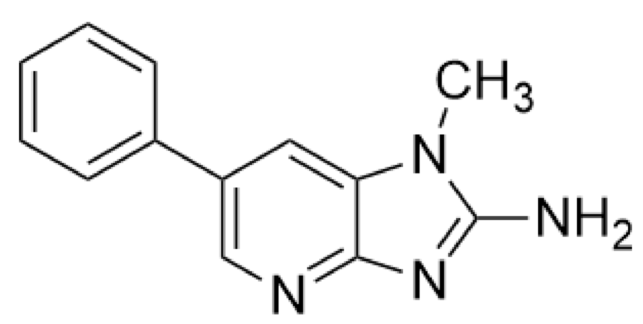
Lillian G. Ryan, Karl J. Feierabend

Department of Chemistry, The College of Wooster

Background

- The Maillard reaction is responsible for the browning of foods during cooking via the formation of large, conjugated molecules from amino acids.
- 2-Amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) is a carcinogen that forms at ppb levels in cooked meat through a Maillard reaction process.
- A recent study[1] found N-containing heterocyclic Maillard products may be selectively degraded by UV
- Research goal: Understand the photoreactivity of PhIP and determine if UV can be used to remove it from cooked food.



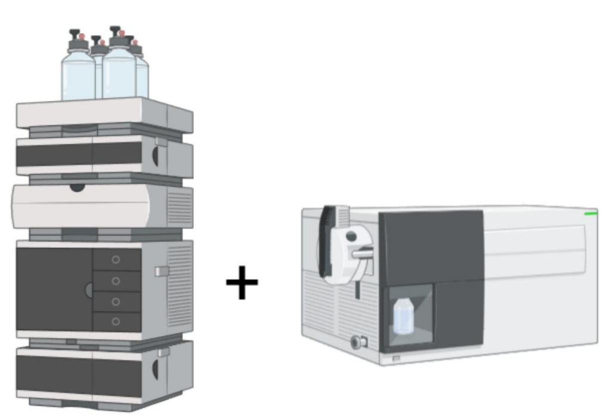


PhIP

Methods

Solutions of phenylalanine, creatinine, and dextrose were heated at 200°C to generate PhIP. Plain aqueous and Maillard-mixture PhIP were exposed to UV-B (280-320 nm) light in a photoreactor for various time increments.

UV-B Photoreactor



LC-QQQ-MS

PhIP concentration was measured using Liquid Chromatography-Mass spectrometry (LC-MS) using caffeine as an internal standard.

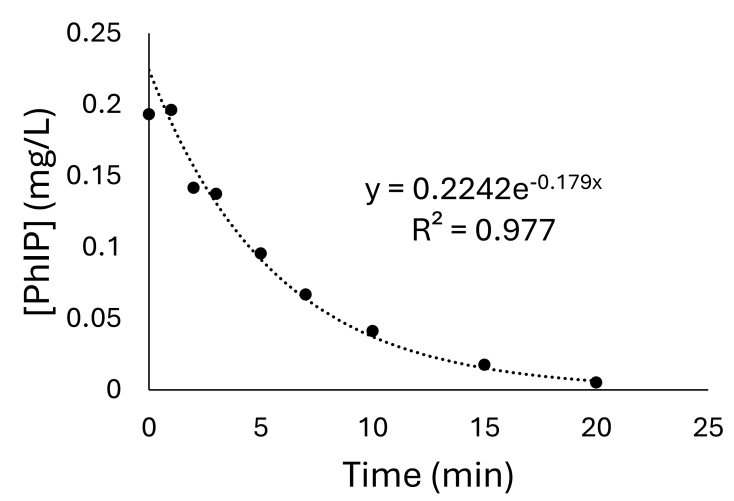
Gaussian16 software[2] was used model PhIP before and after absorption of UV-B. Associated energies were calculated using density functional theory (DFT). An implicit solvation model was used to simulate aqueous surroundings.

Gaussian, Inc.

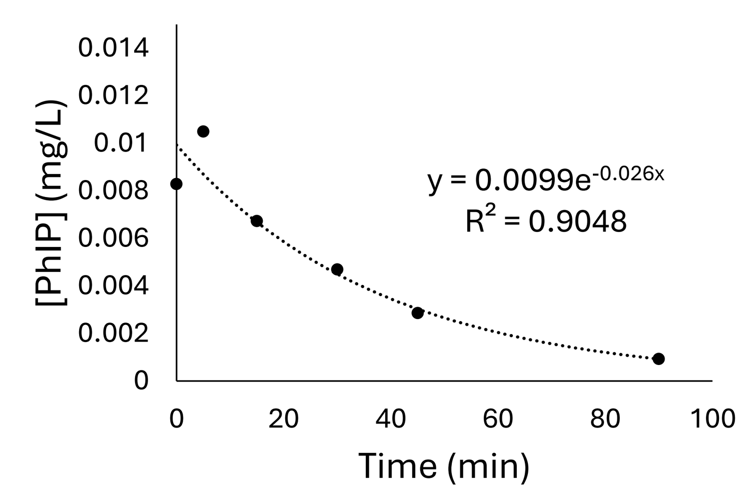
Results and Discussion

Photodegradation Kinetics

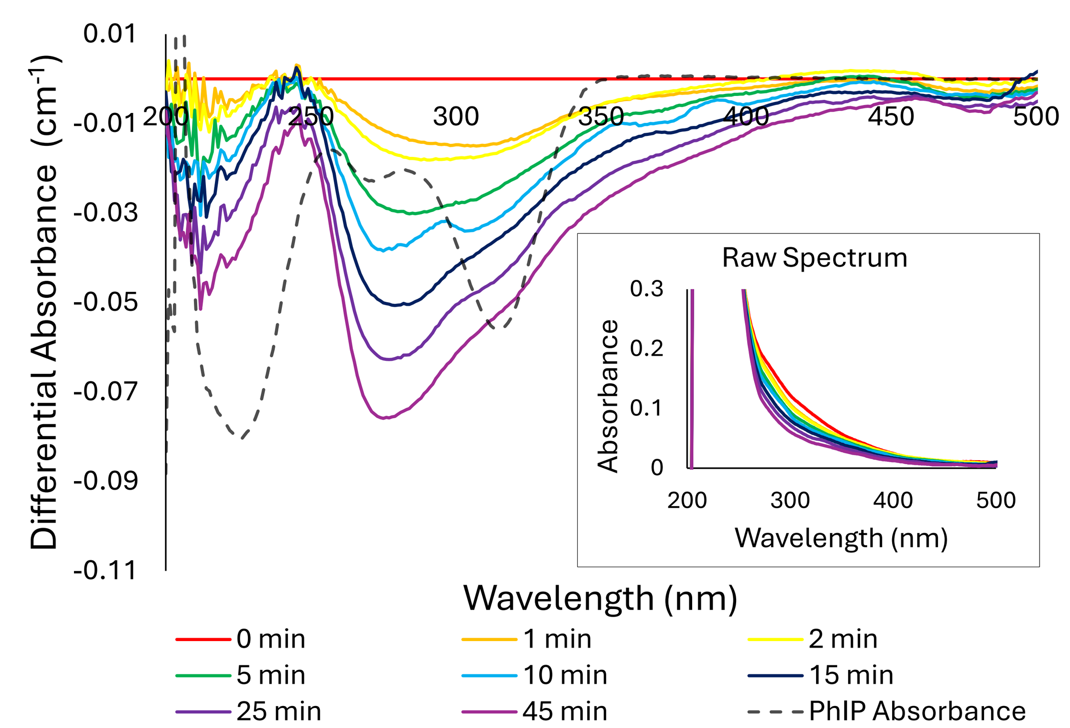
PhIP in Water



PhIP in Maillard Mixture



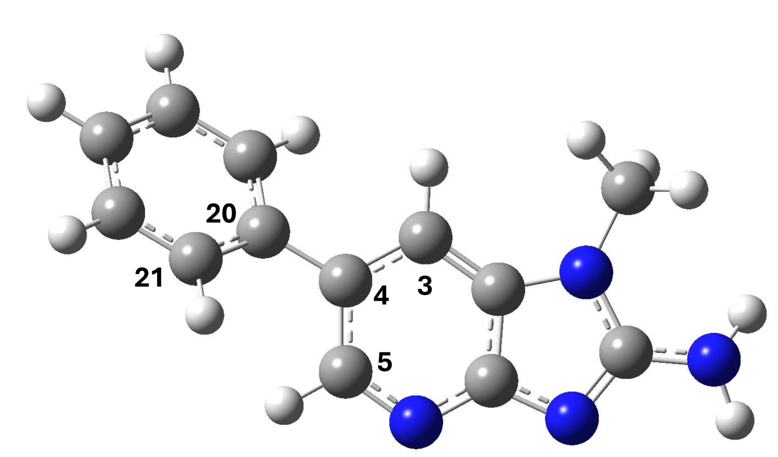
Maillard Mixture Spectral Change

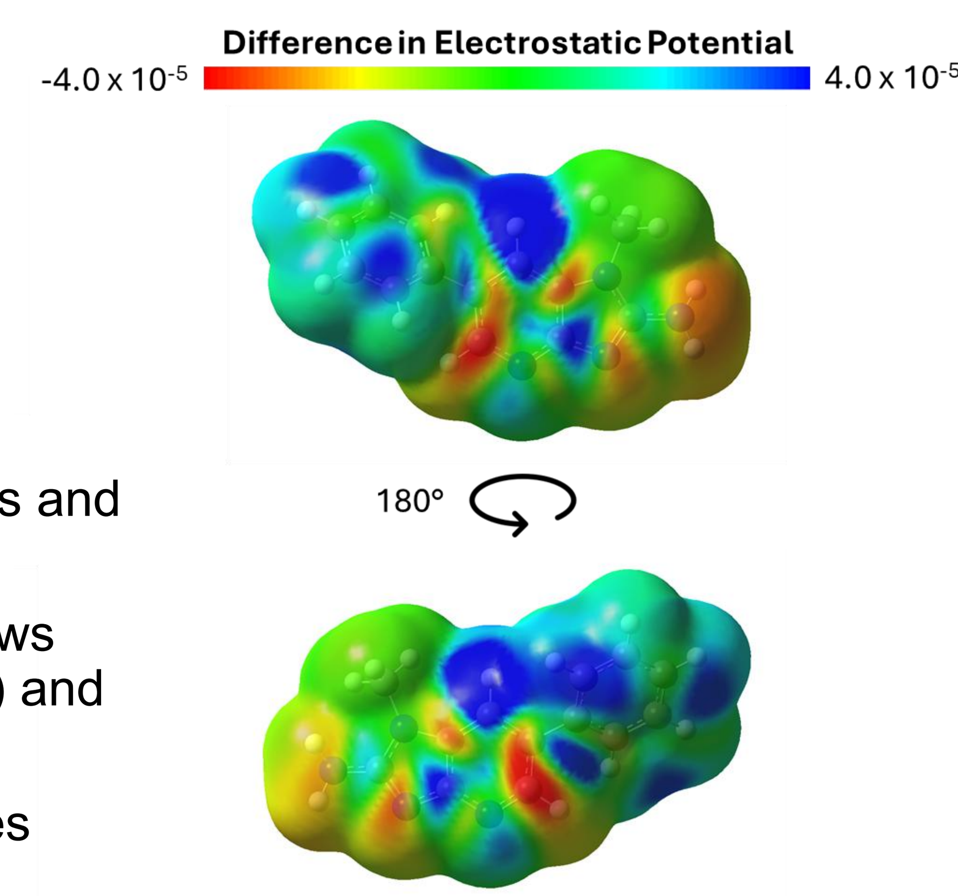


- Observed first order kinetics with respect to PhIP concentration
- 7-fold decrease in rate of photodegradation in the presence of other Maillard reaction products
- Full absorbance spectrum shows selectivity of photolysis towards specific compounds in mixture around PhIP absorbance peaks

Computational Results

3D Geometry (S0)





- Geometric changes: 4,3 bond elongates and weakens on excitation
- Difference in electrostatic potential shows where electron density increases (blue) and decreases (red) on excitation
- Polarization across central ring indicates susceptibility to attack by oxidizing or reducing species when absorbing UV

Conclusions

So, photolysis happens. But how efficiently?

Sample	k_{obs}(min^{-1})
PhIP in Water	0.179 ± 0.007 min^{-1}
PhIP in Maillard Mixture	0.026 ± 0.002 min^{-1}
Actinometer[3] SMX in Water	0.123 ± 0.001 min^{-1}

Effective Quantum Yield: 0.0021 ± 0.0001

- Effective quantum yield represents ratio of photons absorbed to reactions occurred, with PhIP reacting once per 480 photons absorbed
- Under an 80 W UV-B industrial lamp for 20 minutes: Approximately 97.5% of PhIP in water will degrade, while only 40.5% of PhIP in the Maillard mixture will degrade in that time
- Clues to mechanism: first order kinetics and propensity to react demonstrated from computational model lend evidence to direct photolysis

Future Work

- Determine kinetics of photodegradation in an actual meat patty model
- Control dissolved oxygen content in solution to determine impacts of indirect photolysis
- Improve computational model using hybrid solvation model

ACKNOWLEDGMENTS

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2. Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 3rd ed.; Gaussian Inc., 2015.
3. De Brito Anton, L.; Silverman, A. I.; Apell, J. N. *Environ. Sci. Processes Impacts* **2024**, *26* (6), 1052–1063.