Colorado State University
Fort Collins, CO

Chemical Kinetics – Decomposition of the Benzenediazonium Ion

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Physical Chemistry Laboratory - I
CHEM 475 – L01, L02, & L03
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Chemical Kinetics

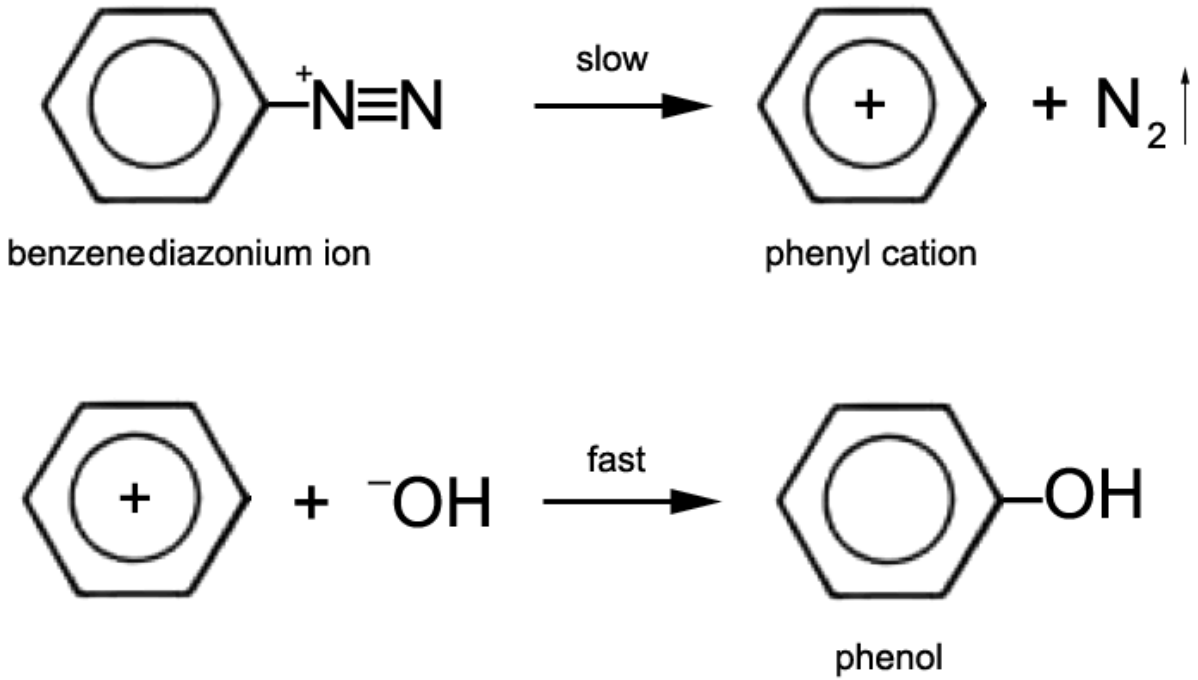
- The study of the rates of chemical processes
  - Especially rates of chemical reactions.
- Can reveal information on reaction details
  - Reaction mechanism and transition state.
- Experimental determination of reaction rates.
  - Rate laws and rate constants can be derived.
- Temperature dependence of rate constant yields activation energy through use of Arrhenius Equation

$$k = A\, e^{-E_{activation}/RT}$$

Method of Determination

- A reaction rate is determined by monitoring the concentration of a product or reactant as a function of time.
  - Increase of [product]
  - Decrease of [reactant]
  - Or both
- Begin with mixture of pure reactants.
- Sample reaction mixture periodically.
- Plot [ ] versus time:
  - Determine reaction rate.
  - Vary initial reactant(s) concentration.
  - Determine reaction order.

Decomposition Reaction



- First order kinetics in dilute aqueous acidic solution
- Easily followed by UV spectrophotometry

An Exciting Experiment

The diazonium salt that should be used in this experiment is benzenediazonium fluoborate ($C_6H_5N_2BF_4$, $M = 191.9$). The great majority of diazonium salts are notoriously unstable solids and can decompose with explosive violence. The fluoborates are by far the safest to use and are not known to explode; however, reasonable caution should be used in preparing the compound. Since even benzenediazonium fluoborate will decompose slowly, it should not be prepared too far in advance, and it must be stored in a refrigerator. A simple high-yield procedure for its preparation has been given by Dunker, Starkey, and Jenkins.[5] Recrystallization of the product from 5 percent fluoboric acid yields white needlelike crystals, which can be dried by vacuum pumping at 1 Torr for several hours.†

EXPERIMENT 23

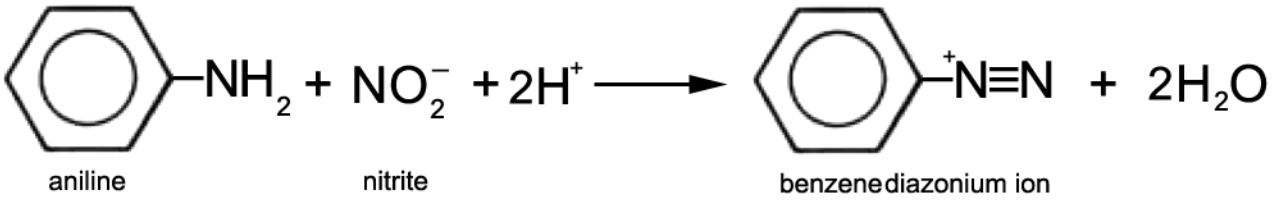
Kinetics of the Decomposition of Benzenediazonium Ion

EXPERIMENTS IN PHYSICAL CHEMISTRY

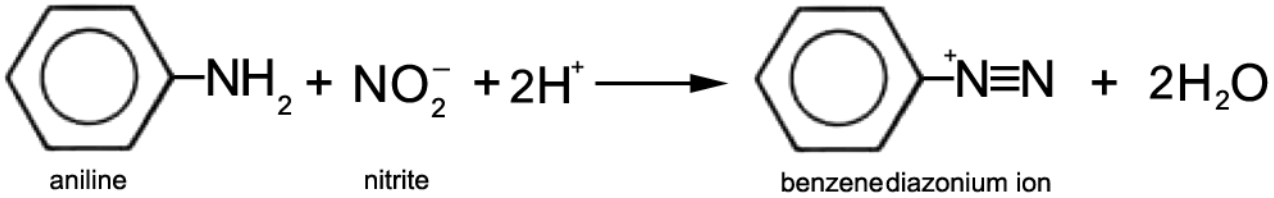
EIGHTH EDITION

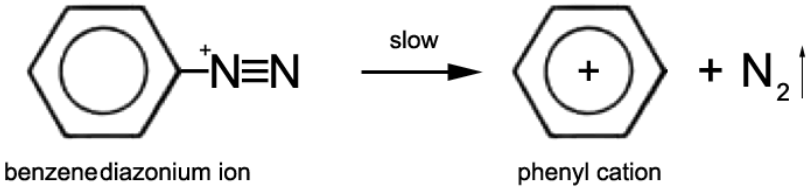
CARL W. GARLAND, *Massachusetts Institute of Technology*
JOSEPH W. NIBLER, *Oregon State University*
DAVID P. SHOEMAKER, *(deceased) Oregon State University*

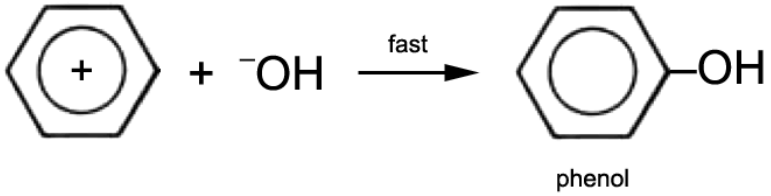
Synthesis Reaction



Combined Synthesis & Decomposition







Practical Matters

- Stock solutions used:
  - 2 mM aniline in 200 mM HCl
  - 2 mM $NaNO_2$ (in water)
  - 2 mM phenol in 200 mM HCl
  - 100 mM HCl (in water)

- By mixing suitable volumes of these solutions
  - Standard spectra of reactants and products and
  - Suitable reaction mixtures can be obtained.

- All measurements are made in 100 mM HCl.
- Standard spectra are made at 0.2 mM.

More Practical Matters

In one flask:

1 mL aniline in 200 mM HCl

8 mL 100 mM HCl

In another flask:

1 mL $NaNO_2$

Equilibrate in water bath.

Mix at “time zero”

Rinse and fill cuvette.

Record UV-Vis spectra.

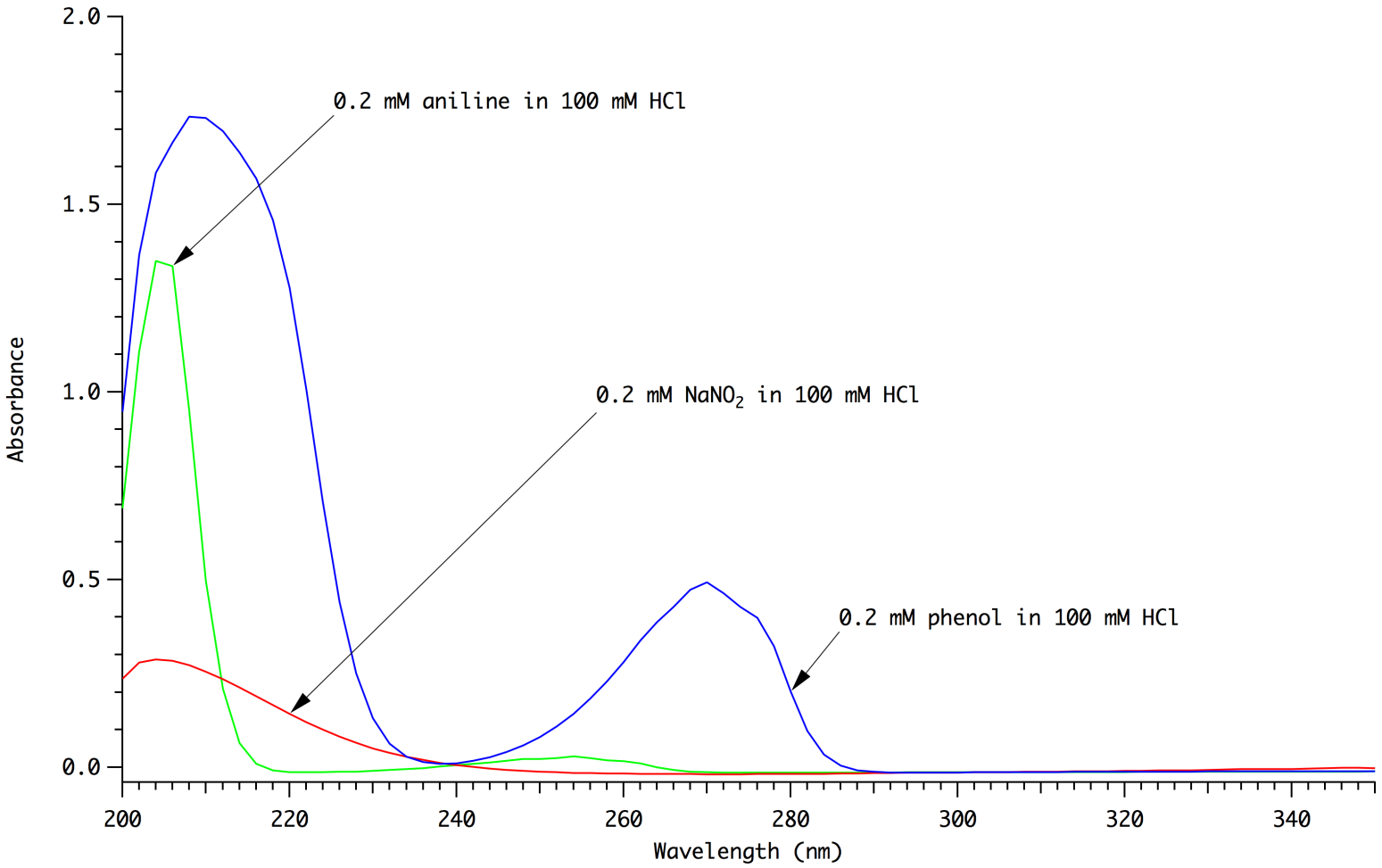
Initial reactant concentrations:

0.2 mM aniline

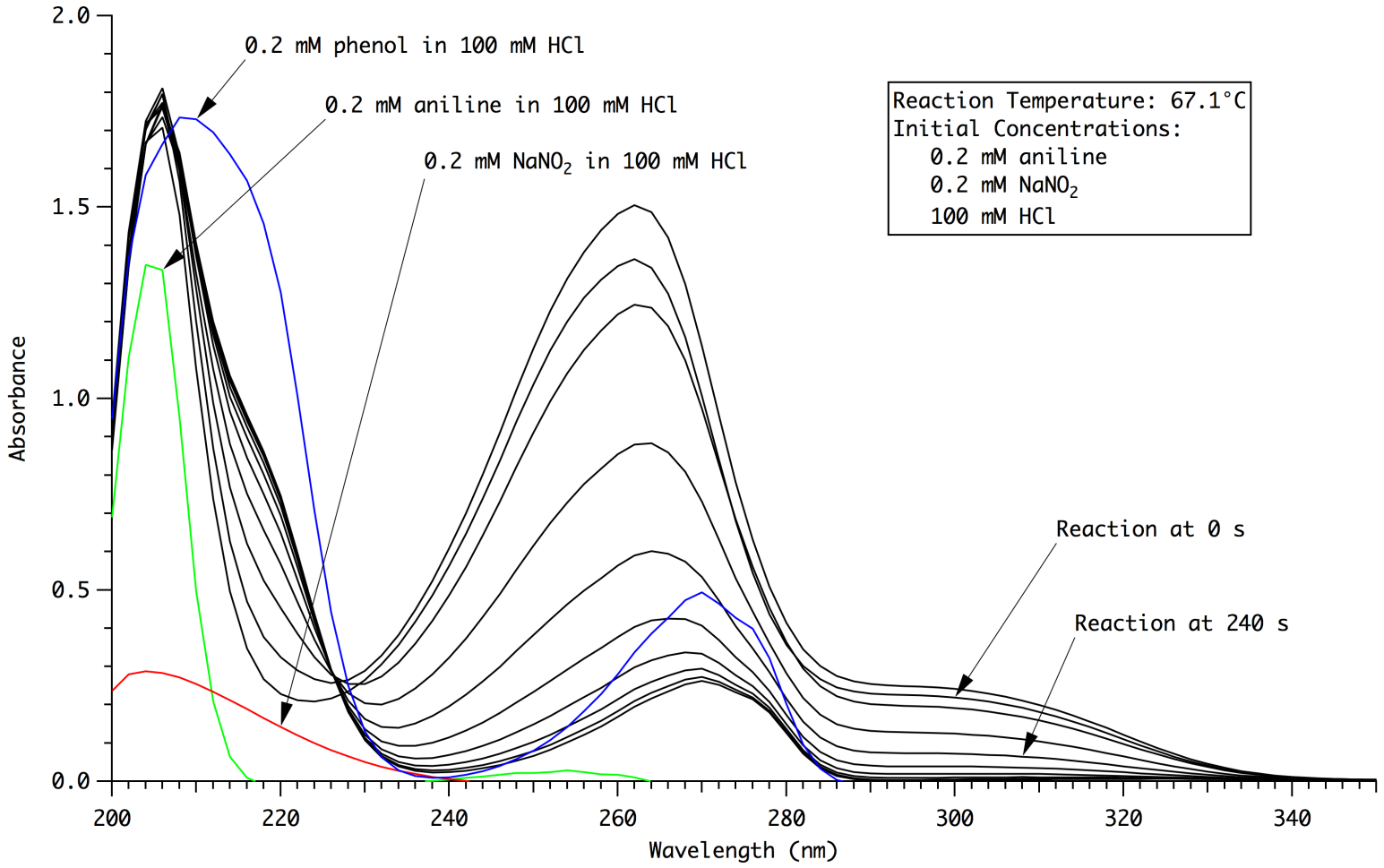
0.2 mM $NaNO_2$

100 mM HCl

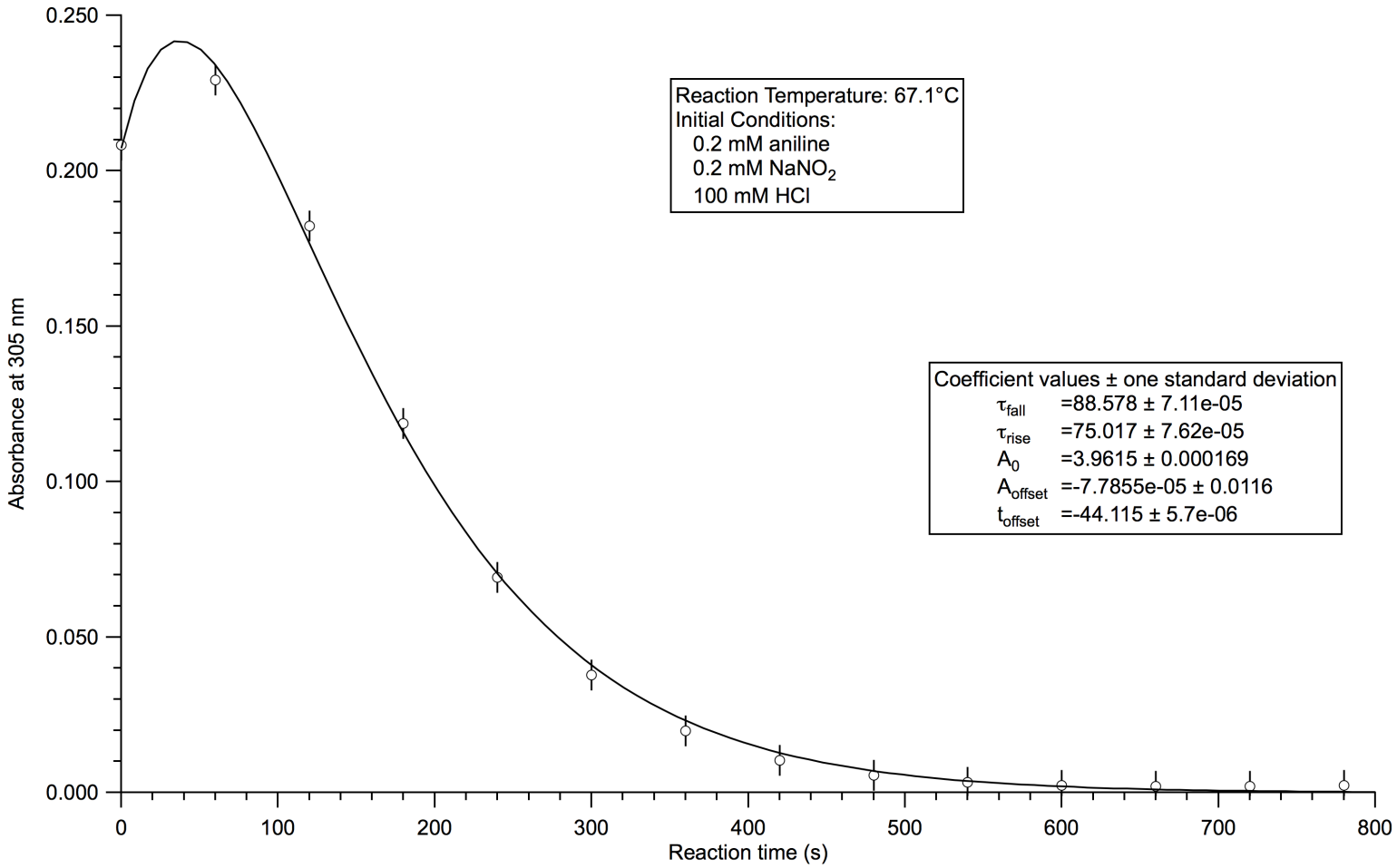
Spectra of Reactants and Product



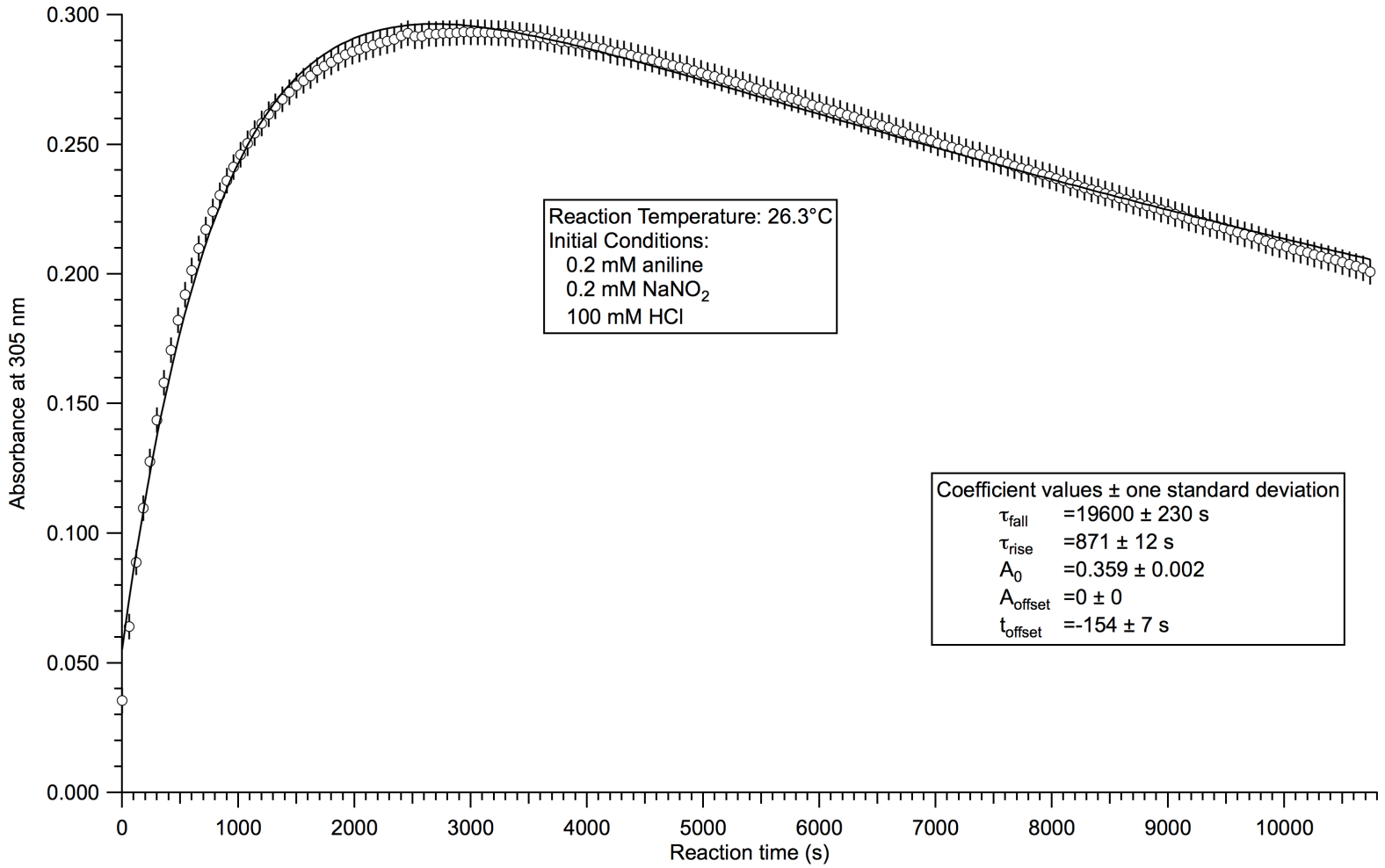
67.1 °C Reaction Spectra



67.1 °C & 305 nm Time Profile



26.3°C & 305 nm Time Profile



Conclusions

- Off to a good start.
- There are additional temperature data to analyze.
- Comparison of existing data with literature values is OK.
  - Could be better…
- Need to synthesize pure diazonium salt for spectrum.
- Measurement of other reaction components.
  - Use multivariate spectral analysis to fit entire data set.