Dediazoniations in Water: An Integrated Physical Organic Chemistry Experiment

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Arenediazonium salts, ArN_2^+, are among the most useful and versatile chemical compounds in fundamental and applied research (*1*). They are widely used in the dyestuff industry and in many synthetic procedures as both intermediates and precursors. Most undergraduate organic chemistry textbooks (*2*) include sections where their chemistry is disclosed, showing arenediazonium salts as ionic compounds in which the diazo group is bonded to an aromatic residue so that the diazonium ion is the appropriate cation. Structures of reactants and products are frequently the principal examples that those textbooks employ to describe arenediazonium chemistry, but even in the best texts, little room, if any, is given to describe how fast the reactions take place (i.e., their rate constants). This causes difficulties to students who fail to recognize the relationships between different branches of chemistry like organic and physical chemistry and may also cause problems to students because they have no intuition about reaction rates and, consequently, about the stability of the compounds.

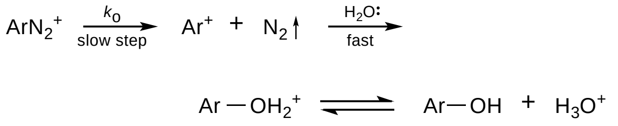
Scant attention has been paid to the use of arenediazonium salts in undergraduate laboratories and very few experiments concerning arenediazonium chemistry (*3*) have been published. Here we propose an integrated physical organic experiment that includes synthesis of an arenediazonium salt as the tetrafluoroborate and a kinetic study of its stability in water.

- **CAUTION:** Some of the chemicals in this experiment are classified as very dangerous, so safety procedures must be reviewed before attempting the experiment.

The experiment fits into the undergraduate physical chemistry (kinetics) or organic chemistry curriculum and can be easily adapted to a number of different laboratory settings. In an open laboratory system, the same student can do both the synthesis and the kinetics. In a traditional laboratory, the compound can be synthesized in advance by organic students and the kinetics portion can be used as a physical chemistry laboratory experiment. Alternatively, the physical chemistry instructor can easily prepare enough of the arenediazonium salt (it can be kept with little decomposition for months under appropriate conditions: dark, dry atmosphere, and low temperature) and students will study its stability. The experiment can also be easily adapted to settings such as the instrumental laboratory.

If the instructor adopts the complete experiment, the students will isolate the arenediazonium salt in the solid state and study its decomposition in water by employing UV–vis spectroscopy and potentiometry. Students will learn synthetic procedures and kinetics and mechanisms of organic reactions. Complementary topics include estimation of product yields and identification of either the diazonium salt or the dediazoniation products, according to instrument availability and the instructor's requirements.

The synthesis is done under anhydrous conditions yielding a crystalline solid arenediazonium tetrafluoroborate salt with yields usually higher than 80%. Stock solutions must be freshly prepared in hydrochloric acid (pH ~ 4) to minimize diazotate formation, and used either immediately or shortly after preparation (with storage in an ice bath) to minimize decomposition. Before doing the kinetics study, students will have to obtain the UV–vis spectra of the arenediazonium salt and the expected products (mainly the phenolic derivative, ArOH), to choose an appropriate wavelength for monitoring dediazoniation so that interferences by dediazoniation products are minimal. A check of the Beer–Lambert law at the chosen wavelength is highly recommended. Published UV–vis spectra of a number of arenediazonium salts (*4*) show a broad absorption band in the 220–300 nm region, with molar absorptivities of $\varepsilon \sim 10^4\ M^{-1}\,cm^{-1}$, which are strongly dependent on ring substituents and their position. The ortho and meta series show two bands, a main one around 270 nm ($\log \varepsilon \sim 4.0$) and a shoulder around 300–350 nm ($\log \varepsilon < 3.5$). The para series show a single band in the range of 260–380 nm ($\log \varepsilon > 4.0$). Kinetics experiments are initiated by adding an aliquot of the arenediazonium stock solution (no more than 100 µL is recommended, to minimize temperature changes) to the thermostated cell to give final ArN_2^+ concentrations of about 10^{-4} M. Potentiometric measurements require higher arenediazonium salt concentrations, $[ArN_2^+] \sim 10^{-3}$ M, to obtain a significant $[H_3O^+]$ variation that leads to a change of at least one pH unit. By monitoring the disappearance of starting material, ArN_2^+, and by monitoring product formation (H_3O^+ and indirectly the phenol derivative) (Scheme I), students can obtain rate constants for ArN_2^+ loss and H_3O^+ formation. Comparison of the two rate constants will allow students to identify the slow step of the reaction. Comparison of the UV–vis spectrum of dediazoniation products with that of commercial samples of known concentration will allow students to identify the products and obtain product yields. This information can also be obtained from the final pH value (i.e., pH when dediazoniation is complete).



$$ArN_2^+ \xrightarrow[\text{slow step}]{k_0} Ar^+ + N_2\uparrow \xrightarrow[\text{fast}]{H_2O:}$$

$$Ar{-}OH_2^+ \rightleftharpoons Ar{-}OH + H_3O^+$$

Scheme I
the heterolytic $D_n + A_n$ dediazoniation mechanism

We have chosen *o*-methylbenzenediazonium tetrafluoroborate, OMBD, as a representative substrate. Figure 1 shows its spectrum and that of the dediazoniation products in water in the 200–400 nm region. The spectrum of the dediazoniation products is virtually identical to that of an aqueous solution of *o*-cresol, ArOH, of the same concentration as that of OMBD, indicating that under our experimental conditions, only one dediazoniation product, *o*-cresol, is formed almost quantitatively, in agreement with literature reports (*5*, *6*) for a number of arenediazonium salts.

Figure 2 shows the change of absorbance with time due to disappearance of OMBD (monitored at λ = 310 nm) and the corresponding logarithmic plot (Fig. 2A), and the change of $[H_3O^+]$ with time and the corresponding first-order plot at 25 °C (Fig. 2B). The potentiometric observed rate constant, $k_0 = (2.1 \pm 0.1) \times 10^{-4}\ s^{-1}$, is in agreement with that obtained spectrophotometrically, $k_0 = (2.1 \pm 0.1) \times 10^{-4}\ s^{-1}$ and with a literature value of $k_0 = 2.2 \times 10^{-4}\ s^{-1}$ obtained by N_2 evolution (*5*). From the intercept of the first-order plot (Fig. 2B), one can estimate the difference between final and initial concentrations of hydrogen ions, that is, $[H_3O^+]_\infty - [H_3O^+]_0 = [ArOH] = 1.46 \times 10^{-3}$ M, which indicates that yields of ArOH are close to 97%, in agreement with published results (*6*).

This observation can be employed to gain information about arenediazonium chemistry, since the increase in acidity prevents side reactions (*7*) like the coupling of ArN_2^+ with ArOH (which is a dediazoniation product) to yield the corresponding azo dye (addition reaction).

In conclusion, this integrated physical organic experiment presents an opportunity for students to synthesize arenediazonium salts, to perform some easy kinetics experiments, and to estimate product yields from dediazoniations in water. Since diazonium salts are very important for both industry and organic synthesis, this experiment should be more interesting to the students than simpler, less meaningful kinetics experiments. The complete experiment was carried out by a number of undergraduate students who had completed organic and kinetics courses. The synthetic section can be done within 4 hours and the kinetics portion can be completed in a similar time period. A range of temperatures can be used in the kinetics experiments, depending on the nature of the arenediazonium salt or instructor requirements. For example, activation energy for OMBD has been reported (*6*) as $E_A = 108.2\ kJ\ mol^{-1}$; therefore its half-life at 35 °C is only 11 min, allowing performance of as many as four runs in the same time period (~250 min) as one run at 25 °C.

A more complete integrated experiment can be developed if the instructor divides the students into a number of small groups. Each group can synthesize a different arenediazonium salt and study its stability either spectrophotometrically or potentiometrically. After all students complete their experiments, the results can be put together to discuss, with the instructor's supervision, the effects of substituents on dediazoniations (*1a*, *6b*).

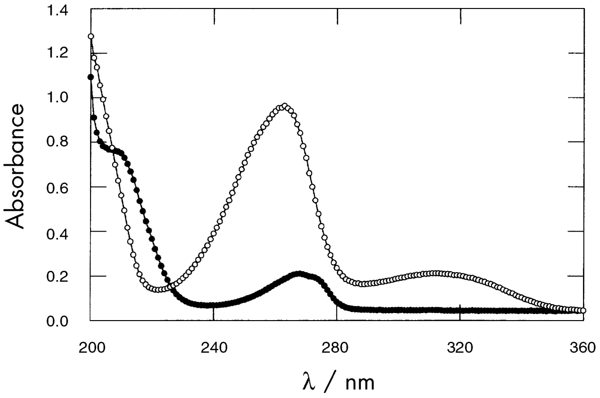


Figure 1. UV–vis spectrum of (○) an aqueous OMBD solution, [OMBD] = 8.40 × 10^{-5} M, [HCl] = 1.0 × 10^{-4} M; and (●) of dediazoniation products.

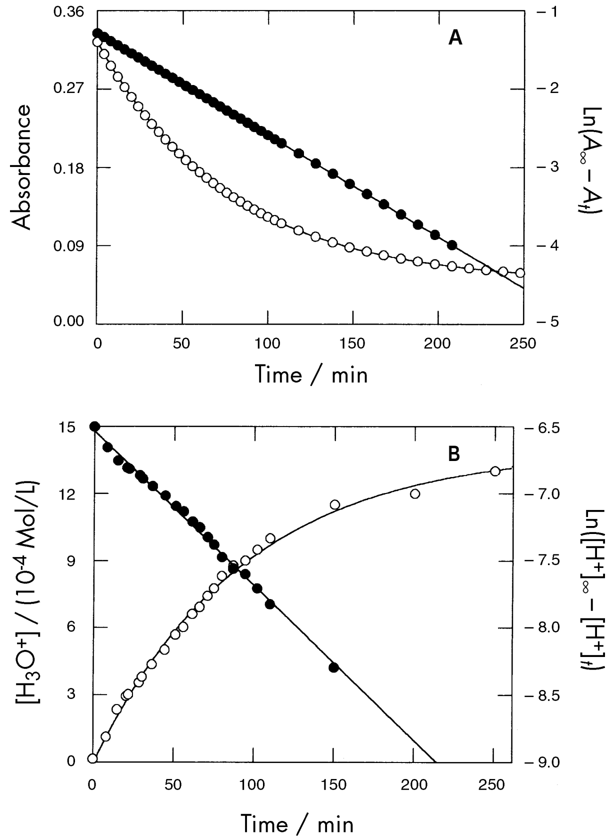


Figure 2. A: (○) Variation of absorbance (λ= 310 nm) with time and (●) ln plot of the data; [OMBD] = 2.3 × 10^{-4} M, [HCl] = 1.0 × 10^{-4} M, *T* = 25 ºC. B: (○) Variation of $[H_3O^+]$ with time and (●) first-order plot; [OMBD] = 1.5 × 10^{-3} M, *T* = 25 °C.

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WSupplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

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