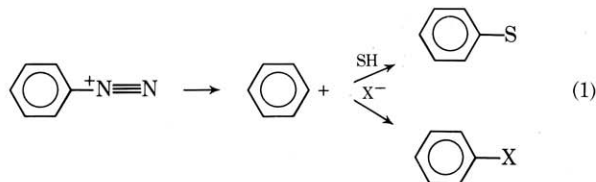


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Hydrolysis of Benzenediazonium Ion

An experiment in first-order kinetics

Decomposition of benzenediazonium ion in acidic media has long (1) been interpreted as proceeding via an S_N1 mechanism in which phenyl cation is generated in the rate-determining step. Subsequently, the phenyl cation reacts with very low selectivity with solvent or nucleophiles (eqn. (1)). Small increases in



rate in the presence of high concentrations of nucleophilic anions have been interpreted (2) as evidence for nucleophilic participation of these anions. In the absence of good nucleophiles, however, the rate of the reaction is very insensitive to the nature of the solvent (3), indicating the absence of appreciable nucleophilic participation by the solvent.

In acidic media, benzenediazonium ion reacts according to strictly first-order kinetics. Since the rate of the reaction is virtually unaffected by the presence of impurities and the reaction has a convenient half-life and large activation energy, it is ideal for study in the undergraduate laboratory.

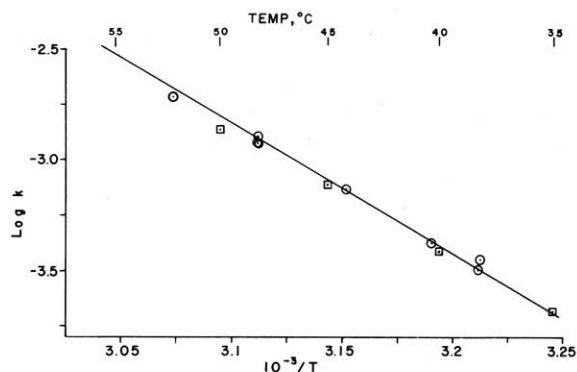
The kinetics of the hydrolysis of benzenediazonium ion may be followed by measurement of the volume of evolved nitrogen. A capillary method for measurement

of nitrogen evolution has been described in THIS JOURNAL by Gesser (4); the rate constants determined by this method were 40–100% higher than those determined by other workers, perhaps because of supersaturation of the solution (5). Alternatively, the amount of the unreacted benzenediazonium ion can be determined by measurement of the absorbance at 295 nm, where the starting material has an extinction coefficient of 1800 and the products are essentially transparent.

A more convenient procedure for the undergraduate laboratory is to couple the unreacted diazonium ion with 2-naphthol-3,6-disulfonic acid, disodium salt (R salt) (6), which gives an orange azo compound, $\lambda_{\max} = 490$ nm ($\epsilon 2.5 \times 10^4$). Since the hydrolysis reaction is thereby quenched, absorbance measurements can be made independently of the sampling, and the cell compartment of the spectrophotometer need not be thermostatted. The azo compound absorbs in the visible region, thus a simple colorimeter or visible spectrophotometer may be employed.

Reagents

Benzenediazonium fluoborate is prepared by diazotization of aniline in fluoboric acid (7). Excess nitrite is destroyed with urea, then the precipitate is filtered and washed with cold 5% fluoboric acid. The material is recrystallized by dissolving in acetone at 20–25°, adding sufficient chloroform to produce cloudiness and chilling in an ice-salt bath; the fine white needles are collected, washed with chloroform, and dried under vacuum.



Rate of hydrolysis (sec^{-1}) of benzenediazonium ion in dilute aqueous acid. The line is the best fit of the data of reference (8).

Impure samples of benzenediazonium fluoroborate deteriorate in a few days, but samples purified in the above manner have been stored in a desiccator at 0–5° for over a year without appreciable decomposition. 2-Naphthol-3,6-disulfonic acid disodium salt (Matheson, Coleman, and Bell reagent grade) may be used without purification.

Kinetics

A 50-ml flask of dilute sulfuric or hydrochloric acid (0.01 to 0.1 *M*) is allowed to equilibrate for 25 min in a constant temperature bath maintained at a temperature between 35° and 55°C. Meanwhile a 13 to 19-mg sample of benzenediazonium fluoroborate is measured into a dry 100-ml volumetric flask, which is then placed in the bath. After a few minutes for temperature equilibration of the flask, the acid is added and the salt is dissolved with vigorous agitation. Samples of the solution are removed at appropriate intervals via dry 2-ml pipets which have been stored in a test tube immersed in the bath (to bring them to the temperature of the reaction). The samples are rapidly added to a 100-ml volumetric flask containing 10 ml of a chilled solution of 0.01 *M* R salt in 0.2 *M* sodium bicarbonate. After standing for 10 min at room temperature to allow completion of the coupling reaction, the solution is acidified with 1 ml of 1 *M* acetic or sulfuric acid. The flask is shaken to promote CO_2 evolution, then diluted to the fiducial mark. The infinity point sample is prepared from 2 ml of the dilute acid or a sample of the reaction mixture from the previous day's kinetic run.

The absorbances were measured at 490 nm on a Bausch and Lomb Spectronic 20 or Beckman DU spectrophotometer. Either

air or the infinity point sample was used for the reference. The solutions deteriorate on standing, but satisfactory measurements may be obtained for up to one week if the solutions are stored in the dark.

Half lives, which can be calculated from the data below, are ~30 min at 40° and 8 min at 50°. During the first half-life samples were taken at 5-min intervals at 40° and at 1½ to 2-min intervals at 50°. Samples were taken at less frequent intervals later in the reaction until 10 to 12 samples had been taken. At temperatures above 38°, the absorbances were measured after sampling had been completed; alternatively, the experiment was performed by students in pairs, one student doing the sampling and the other performing the absorbance measurements. Near 35°, the reaction is sufficiently slow that absorbance measurements could be made between samplings.

Results

This experiment has been performed successfully by students in an honors section of first year chemistry and in an instrumental analysis course. Typical student data gave coefficients of variation for the rate constants of about 5% according to a nonlinear least-squares computer analysis of the kinetic data. The reproducibility of rate constants at a given temperature was 5–10% depending on the equipment used. Above 50°, the reaction was rapid and timing and temperature errors become very significant. Below 35°, the reaction is tediously slow. Activation energies calculated from various sets of data ranged from 25.2 to 28.6 kcal/mole, in agreement with the reported values of from 27.1 to 28.2 kcal/mole. The figure shows an Arrhenius plot for several sets of data.

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