Fading of Bromophenol Blue
A combined synthesis and spectrophotometric kinetics experiment

In recent years it appeared desirable to have a kinetics experiment for students in the second term of our integrated laboratory sequence. This course—with approximately 100 chemistry and biochemistry students—is primarily oriented toward analysis of organic and inorganic systems with emphasis on instrumental methods; background chemistry, theory, and general techniques are discussed in two lecture meetings each week. Instructionally it was useful to have an experiment in which students would synthesize and purify their compound and measure a reaction to apply the principles of spectrophotometry and kinetics discussed in lecture and readings; at this point the students had experienced quantitative analysis of unknowns using UV-visible spectrophotometry. A constraint was placed upon the experiment by the fact that only the single beam visible spectrophotometers (Spectronic 20) were available in sufficient numbers to avoid dislocations in scheduling occasioned by instrumental breakdown.

In this context we have developed an experimental sequence involving synthesis of phenolsulfonphthalein, bromination of this to give bromophenol blue, and study of the fading of the latter in strongly alkaline medium. Data analysis was performed with both graphical and computer techniques. The experiment encompasses the following features:

1) A two-step synthetic sequence is involved in which the students gain experience in handling moisture-sensitive (fused ZnCl2) and corrosive (Br2) reagents.
2) Both phenolsulfonphthalein and bromophenol blue are commercially available; students who lose a product through accident may complete the experiment within the time schedule.
3) The experiment relates well to lecture discussions of indicators, aromatic substitutions, and kinetics; several kinetic topics are involved (vide infra).
4) The fading reaction obeys second-order kinetics but is carried out under pseudo first-order conditions (large excess of base); the second-order rate law is emphasized by examination of fading at varying concentrations of base. The reaction is, in fact, an approach to equilibrium; however, the equilibrium lies sufficiently toward product that the graphical treatment is not computationally laborious.
5) Data analysis by "classical" graphical and "modern" computer methods is experienced and compared.
6) The fading rate is sufficiently high to allow the reaction to be followed over several half-lives during a single laboratory period.

Background

Triphenylmethane dyes of the phthalein and sulfonphthalein type (II) are generally prepared by interaction of the appropriate anhydride (I) with phenolic compound in the presence of an acid catalyst (H2SO4, anhydrous ZnCl2) (I).

$\text{X} = \text{CO or SO}_2$. Form (II) exists in strong acid only; in more weakly acidic medium these compounds exist in the ionized form (III) which is converted to (IV) as the pH is raised to the vicinity of the $pK_a$; the transformation is generally accompanied by a marked change in color, making these compounds highly useful as acid-base indicators (2).

$Y = \text{H or Br}$. By varying $X$ and the structure of the phenolic rings—relatively simple, synthetic modifications—both the absorption maximum (color) and the pH region of the color change may be varied considerably (3). Further increases in pH eventually convert (IV) to the deconjugated colorless trianion (V); this reaction is responsible for the "fading" of these indicators at high pH.

Discussion

Students prepared phenolsulfonphthalein (phenol red) by reaction of (I) ($X = \text{SO}_2$) with phenol in presence of freshly fused ZnCl2 by a procedure modified from one described (3) for o-cresol red. The product was brominated
in ethanol (6); acetic acid may also be used (7) but such large volumes are required as to be both uneconomical and malodorous for a large class. The overall yield of this sequence is low but is more than adequate for the measurement. Purity of the product may be assessed from the absorption coefficient determined by the students as an integral part of the kinetics study.

The fading experiment was carried out with two parallel runs at 0.5 and 1.0 M base, the exact base concentrations being determined by titration; students were encouraged to reconfirm the base concentration after completion of the reaction. The half-lives observed for the reaction in 1.0 M and 0.5 M base were approximately 10 and 20 min, respectively, rapid enough to allow the reaction to be followed to at least three half-lives during part of a laboratory period. Phenol red contaminant fades so slowly as to cause no difficulties; the presence of significant quantities of incompletely brominated product made itself felt as a curvature in the rate plot during the third half-life. Experience has shown that even students who performed the synthesis poorly (impure bromophenol blue) were able to obtain satisfactorv data with good agreement (within 20%) of rate constants with those using pure material.

Although (III) is in fact an equilibrium, the equilibrium constant is so large2 that the reaction may be treated as if irreversible, using the expression

$$\ln(A_n - A_{n+1}) = -k_1t + \ln(A_0 - A_n)$$

where $A_n$ = the measured absorbance. The value of $A_n$ was obtained after ten half-lives during the subsequent laboratory period. The value of $A_0$ was obtained using dilute base; the $pH$ required for >99% conversion of (III) ($X = SO_2$, $Y = Br$) (yellow monooanion) to IV ($X = SO_2$, $Y = Br$) (blue diion) is far less than that required for measurable fading of (IV) ($X = SO_2$, $Y = Br$) (pH 6-7 and pH 12-13, respectively).

Depending on the level of sophistication of the students, they may either write their own program (8) or use a file one. We have employed the latter solution with a non-linear least squares program fitting

$$A_n = A_\infty + (A_0 - A_\infty)e^{-k_1t}$$

in which $A_\infty$, $A_0$, and $k_1$ were treated as adjustable parameters.

The quality of data obtained was consistently good considering that temperature control was provided only by ambient air conditioning. As part of their error analysis students were asked to calculate the rate change for a two degree variation in temperature assuming an Arrhenius constant of 13.6.

The overall experiment requires three 3-hour laboratory

2 This is untrue of most phenolsulphonphthalein indicators (6, 7).

3 In contrast, for phenolphthalein the difference is only 1-2 pH units (4).

4 It is necessary to use such a large quantity of ZnCl$_2$ in the fusion although the next step requires only 1.5 per student. The excess can be returned to a bottle for reuse by a later group of students. Use of ZnCl$_2$ which is not very dry is a chief cause of failure in the phenol red synthesis.

5 Inexpensive deep fat fryers were used as oil baths, holding 20-25 tubes in a perforated aluminum cover plate.

6 Bromine reacts slowly with ethanol.

periods. As the full attention of the student is required for only a part of each period, another experiment was assigned concurrently.

**Experimental Procedure**

**Phenol Red**

In a 3-5-in. porcelain evaporating dish was placed 30-55 g of ZnCl$_2$. This was heated until the solid melted (hood!) and then maintained as a melt with stirring (glass rod only) for 5-10 min. The flame was removed and—holding the dish with tongs—the ZnCl$_2$ was stirred rapidly until it solidified as a granular solid; it was then transferred to a mortar and ground quickly to a fine powder.4 The powdered ZnCl$_2$, 1.5 g, and o-sulfobenzoic anhydride, 1.5 g, were mixed without delay in a 16-mm diameter test tube and heated in an oil bath at 150°C for 1 hr.5 The red solid mass was transferred to a 250-ml Erlenmeyer flask with the aid of small portions (to a total of 50 ml) of 10% Na$_2$CO$_3$ solution. After filtration to remove any solid, the resulting wine-colored solution was neutralized by drop-wise addition of 12 N HCl (~12 ml). The volume of the orange-red suspension was reduced in half by boiling (hood!), cooled in an ice-water bath, and filtered with suction to give a deep red solid (phenol red). The yield varied between 0.2 and 0.5 g.

**Bromphenol Blue**

In a 50-ml flask was stirred 200 mg of crude phenol red and 10 ml of absolute ethanol until most of the solid dissolved and then cooled in an ice-water bath. No more than 10 min before use, a solution of 3.6 g (1.2 ml) of bromine (corrosive—severely burns skin) and 9 ml of ethanol was prepared. With cooling, the bromine solution (1.5 ml) was added drop-wise to the phenol red in ethanol; the mixture was stirred at 0°C until no solid remained and then for another 15 min with warming to room temperature. Workup was performed as described for phenol red (Na$_2$CO$_3$ soln., etc.). The product was filtered as pink to deep-red crystals. In some cases additional product was obtained by further acidification of the filtrate; however, excessive addition of HCl resulted in precipitation of NaCl. Yield varied from 150-250 mg.

**Kinetics**

A stock solution of bromphenol blue was prepared from a weighed sample of approximately 50 mg in 100.0 ml of distilled water. Kinetic solutions were prepared just before use by a 2:100 dilution of this stock solution with standardized 0.5 and 1.0 M base. The absorption coefficient was obtained by similar dilution using distilled water and a few drops of base. This dilution (2:100) generally gave an initial absorbance of 0.7 in the standard cuvette of the Spectronic 20 but required adjustment if the bromphenol blue was significantly impure. Runs were made at ambient temperature (~22°C) with readings at approximately 2-min intervals; no problems were encountered by students in carrying out concurrent runs at the two base concentrations.

**Literature Cited**


