

ALKALINE FADING OF ORGANIC DYES: AN IDEAL REACTION FOR HOMOGENEOUS REACTOR EXPERIMENTS

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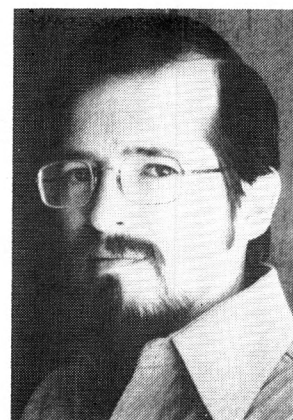
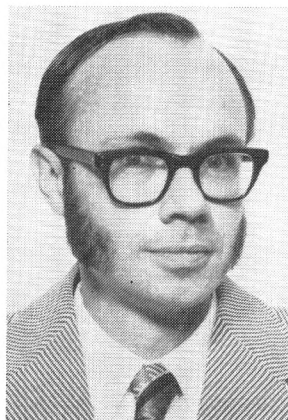
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THIS ARTICLE SUMMARIZES our experience using the alkaline fading reaction of certain organic dyes as a means of introducing students to the behavior of homogeneous reactors.

Since the fall of 1960, the Department of Chemical Engineering at Princeton has had a Chemical Reactor Laboratory as an integral part of its undergraduate curriculum. Initially offered as an elective for seniors in the spring term following a fall lecture course in kinetics of chemical processes, it is now combined with the lecture course and is taken by all departmental seniors. The Chemical Reactor Laboratory owes its existence to the late Richard H. Wilhelm who conceived the idea and provided the inspiration and guidance for its successful implementation. It has been described in some detail by J. B. Anderson [2], who was instrumental in the laboratory's development. The experiences described here were gained not only in the laboratory at Princeton, but also in similar laboratories at the University of Arizona and California State University, Long Beach.

An important component of the laboratory is the study of a single homogeneous reaction in batch, CSTR, and tubular flow reactors as a unified base for comparison and understanding of reactor systems. This concept forms an integral part of many similar reactor labs throughout the country. The reactions most commonly used for this purpose are the hydrolysis of acetic anhydride or

the saponification of ethyl acetate. Data is typically collected by direct sampling and titration. Our experience with this procedure is that about one-third of the groups fail to get acceptable results because of poor planning and poor experimental techniques, and all of the groups become frustrated by the tedium of many titrations. In an attempt to provide a better environment for experimental success and to increase the possibilities for examining various pertinent supplementary effects within the time constraints of the laboratory, we have recently replaced this classic re-



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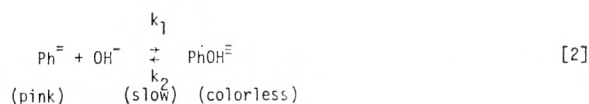
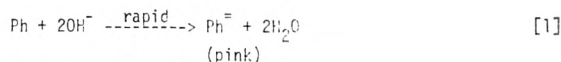
action with the alkaline fading of an organic dye. Use of such a reaction has the following advantages:

- Extent of reaction easily monitored continuously.
- Wide range of rate constants possible.
- Understanding of phenomena reinforced by visualization.
- Minimal safety hazards, waste processing problems, and chemical costs.

While our selection of an "ideal" reaction system for homogeneous reactor experiments is not unique, we feel that it offers considerable advantages that may not be widely recognized.

ALKALINE FADING OF DYES

BROMOPHENOL BLUE, crystal violet, malachite green, and phenolphthalein all undergo a slow decolorization upon combining with hydroxide ion. For example, when phenolphthalein (Ph) is added to an alkaline solution it first undergoes a rapid irreversible conversion to the quinoid form (Ph⁼) which has a pink color (absorbance peak of 550 μ). The quinoid form then slowly and reversibly reacts with hydroxide ion to form the nonresonant (hence colorless) carbinol form (PhOH⁼). Presumably the reactions are:



The kinetics of reaction (2) are conveniently studied by following the decolorization of the reacting mixture using a colorimeter or spectrophotometer. We chose the phenolphthalein reaction because it illustrates a number of important concepts:

1. Coupling of Kinetics and Thermodynamics

Since the reaction is reversible, the coupling of kinetics and thermodynamics is demonstrated. The heat of reaction (from equilibrium studies at various temperatures) can be related to activation energies (from kinetic studies at various temperatures). Also, this reversible behavior adds an interesting additional complexity to the kinetic analysis. Note the other dyes mentioned above fade irreversibly.

2. Rate Determining Step

Since step (1) is essentially instantaneous, the reaction rate is determined solely by step (2).

3. Pseudo-Rate Constant

In practice $[\text{OH}^-] \gg [\text{Ph}]$ (typically 10^{-1}M vs 10^{-5}M) so the concentration of base remains effectively constant over the course of the reaction and a pseudo-rate constant can be defined. This also has the practical advantage of allowing the experimenter to select the time scale of his kinetic runs by suitable choice of hydroxide concentration. A 0.1 N hydroxide concentration provides a "half-life" of about 7 minutes at room temperature while doubling the concentration to 0.2 N shortens the half-life to about 2 minutes.

4. Salt Effect

In reactions between ions the rate "constants" are concentration dependent. The effect of positive ions in the solution is to shield the negative

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charges of Ph⁼ from OH⁻, decreasing the coulombic repulsion of these species and thus increasing the frequency with which they collide. Thus the ionic strength of the reaction mixture has an important effect on the kinetics. The Bronsted-Debye limiting law is helpful for quantifying this effect (ref. (3)).

The use of this reaction in a batch reactor and in a CSTR sequence will be briefly discussed.

ISOTHERMAL BATCH REACTOR

THE EXPERIMENT IS performed in conventional glassware with thermostatic temperature control. The reaction is initiated by rapidly mixing a few drops of phenolphthalein solution (ethyl alcohol solvent) into a dilute aqueous NaOH solution of known concentration and is followed by continuously monitoring on a spectrophotometer the absorbance of the reacting mixture with time. To avoid removing discrete samples for analysis the reaction mixture is recycled through a flow-through cell in the spectrophotometer as shown in Fig. 1. An easily constructed

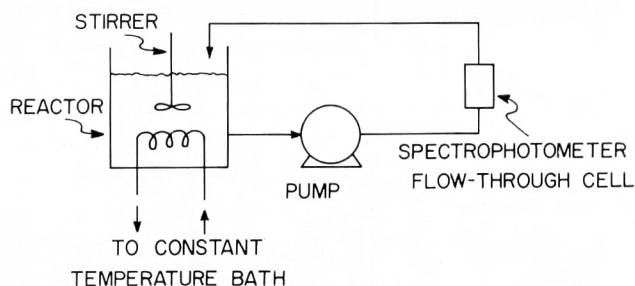


FIGURE 1.

flow-through cell is shown in Fig. 5 (cf. reference (5)). The volume of reacting fluid in the reactor can be quite small; the reactor vessel is really only needed to insure good mixing and temperature control. Care must be taken to avoid forming air bubbles in the recirculating system as this will affect the absorbance of the solution.

Postulating the rate law for reaction [2] to be

$$-r_{\text{Ph}^=} = k_1 [\text{Ph}^=][\text{OH}^-] - k_2 [\text{PhOH}^=] \quad [3]$$

and noting at equilibrium ($t \rightarrow \infty$) that

$$K = \frac{k_1}{k_2} = \frac{[\text{Ph}^=]_0 - [\text{Ph}^=]_\infty}{[\text{Ph}^=]_\infty [\text{OH}^-]_\infty} \quad [4]$$

it follows for the batch reactor, since $r_{\text{Ph}^=} = d[\text{Ph}^=]/dt$

$$\frac{[\text{Ph}^=] - [\text{Ph}^=]_\infty}{[\text{Ph}^=]_0 - [\text{Ph}^=]_\infty} = \exp[-(k_1' + k_2)t] \quad [5]$$

where

$k_1' = k_1[\text{OH}^-]$, pseudo first order rate constant
 $[\text{Ph}^=]_0$ = concentration of colored species at instant of initiation

Note the reaction is within 5% of equilibrium when $t = 3/(k_1' + k_2)$. If the Beer-Lambert law is followed*, concentration is directly proportional to absorbance A and

$$\ln \frac{A(t) - A(\infty)}{A(0) - A(\infty)} = -(k_1' + k_2)t \quad [6]$$

Plotting $A(t) - A(\infty)$ ** vs. t on semilog paper should yield a straight line of negative slope

* This can be tested by finding $A(0)$ (by the extrapolation procedure described) for several levels of $[\text{Ph}]$ (total phenolphthalein concentration in both forms: $\text{Ph}^=$ and $\text{PhOH}^=$). A plot of $A(0)$ vs. $[\text{Ph}]$ should be linear.

** Alternately $A(t) - A(t + \Delta t)$ can be plotted where Δt is a constant time interval. The intercept is then $[A(0) - A(\infty)](1 - \exp[k_1' + k_2]\Delta t)$.

$(k_1' + k_2)$. Figure 2 shows such a plot of student data. Note that $A(0)$ need not be directly measured, it can be found from the intercept of the above plot. The separate rate constants are then extracted by noting from Eq. [4]

$$k_2 = \frac{k_1' + k_2}{K[\text{OH}^-] + 1} \quad [7a]$$

$$k_1 = Kk_2 \quad [7b]$$

where

$$K = \frac{A(0) - A(\infty)}{A(\infty)[\text{OH}^-]} \quad [7c]$$

The heat of reaction may be easily determined by changing the temperature at the end of a run, waiting for a new equilibrium to be established, and measuring the new absorbance $A(\infty)$ (note that $A(0)$ is not affected). A van't Hoff plot of $\ln K$ vs $1/T$ should yield a straight line of slope $-\Delta H_r/R$.

By carrying out kinetic runs at several temperature levels the activation energies and pre-exponential factors can be determined from an Arrhenius plot ($\ln k$ vs. $1/T$). The ionic strength

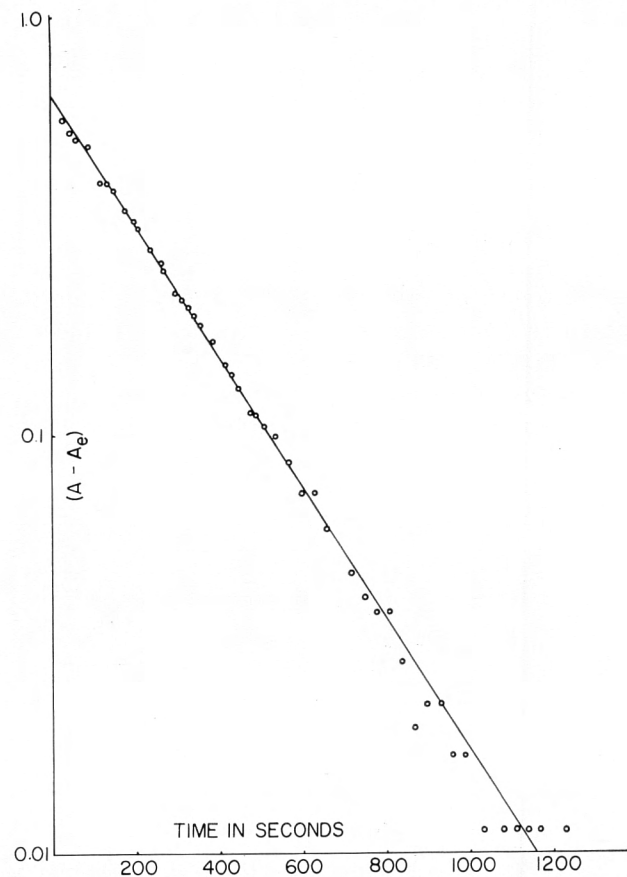


FIGURE 2.

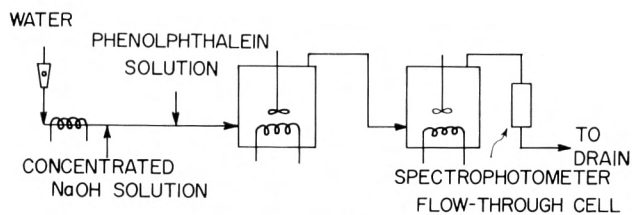


FIGURE 3.

must be the same at all temperatures used in constructing this plot.

The effect of ionic strength can be examined by studying the kinetics using several hydroxide ion concentration levels at a fixed temperature. Alternately an inert salt can be added to raise the ionic strength. An instructive question to ask the students is how they could test the presumed first-order dependence with respect to $[\text{OH}^-]$. Repeating the experimental procedure using several $[\text{OH}^-]$ levels will *not* be sufficient since k_1 is dependent on the ionic strength. A possible way out of this dilemma is to add an inert salt to maintain the ionic strength at the same level in all runs. More detailed information on these reactions is available in references [3] and [4].

CONTINUOUS STIRRED TANK REACTORS

A SERIES OF TWO isothermal stirred tank reactors are used as shown in Fig. 3. Dilution water is fed from a constant-head tank through a rotameter and through a heat exchange coil in a constant temperature bath before entering the first reactor. The NaOH solution is fed by a variable speed metering pump and the phenolphthalein solution by a variable speed syringe pump directly to the first reactor. "Start-up" is studied, in which a step input of phenolphthalein is introduced at $t = 0$. Prior to this the tanks are emptied and the water-NaOH mixture is fed into them at the chosen flow rates so the concentration of NaOH throughout the system is constant during the run. Flow rates, concentrations, and temperatures are selected which will give comparable effects of convection and reaction, i.e., a mean residence time comparable to the "half-life" for reaction. The transient response of the system to the step input of Ph is continuously followed by monitoring the absorbance of the effluent from the second tank. Due to the very low flow rate of Ph solution required, the total flow to the system is not significantly affected by the start up.

Once steady state has been achieved, the effluent from the first tank is diverted through the

flow-through cell using a line which bypasses the second tank. The feed stream absorbance could be similarly measured. Finally a sample of one of the steady-state effluents is allowed to reach equilibrium at the operating temperature and its absorbance is measured. A convenient way to accomplish this is to allow the bypassed second tank to operate as a batch reactor and sample by recycling as described in the previous section. While waiting for equilibrium in the second tank, if the feed of Ph to the first tank is stopped then the transient response to a "shut down" can be continuously monitored.

The unsteady-state material balance assuming ideal CSTR's yields the sequence of coupled linear differential equations:

$$\frac{d}{dt'} \begin{bmatrix} x_1(j) \\ x_2(j) \end{bmatrix} = - \begin{bmatrix} (k_1' \theta + 1) & -k_2 \theta \\ -k_1' \theta & (k_2 \theta + 1) \end{bmatrix} \begin{bmatrix} x_1(j) \\ x_2(j) \end{bmatrix} + \begin{bmatrix} x_1(j-1) \\ x_2(j-1) \end{bmatrix} \quad [8]$$

θ = mean residence time in each tank
(equal volumes assumed); $t' = t/\theta$

$$x_1(j) = [\text{Ph}^-]_j / [\text{Ph}^-]_0$$

$$x_2(j) = [\text{PhOH}^-]_j / [\text{Ph}^-]_0$$

(j denotes tank number; 0 refers to feed stream). For a step input of Ph^- to tank 1 the solution to Eq. [8] can be found by standard methods (cf. ref. (1)) to be

$$x_1(j) = \frac{1}{K'+1} \left[\alpha^j K' (1 - e^{-t'/\alpha}) \sum_{n=0}^{j-1} \frac{(t'/\alpha)^n}{n!} + 1 - e^{-t'} \sum_{n=0}^{j-1} \frac{(t')^n}{n!} \right] \quad [9]$$

where $1/\alpha = (k_1' + k_2)\theta + 1$ and $K' = k_1'/k_2$. The above presumes that initially there is no phenolphthalein in any tank and that negligible conversion to PhOH^- occurs in the feed stream. Since Eq. [9] is somewhat cumbersome students may prefer to solve Eq. [8] numerically on a digital computer. Eq. [9] suggests a convenient form for displaying experimental data: a semi-log plot of $1 - A(j)/A^{ss}(j)$ vs. t/θ where $A(j)$ is the absorbance of effluent from tank j and $A^{ss}(j)$ is its steady-state value (Beer's law assumed). The shutdown case is modeled in an analogous manner.

The rate constants k_1' and k_2 may be obtained from the batch studies described previously if the same conditions of base concentration and temperature are used in this CSTR study. Alternately there is enough information to obtain them

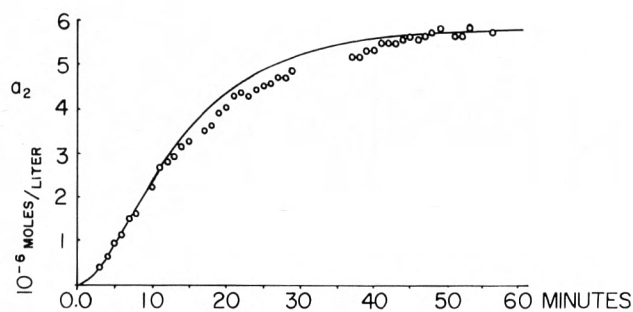


FIGURE 4.

from the steady-state measurements described above since from Eq. [9]

$$x_j^{ss} = \frac{\alpha^j k' + 1}{k' + 1} \quad [10]$$

or rearranging

$$\alpha^{k'} = \frac{A^{ss}(1) - A(\infty)}{A^{ss}(2) - A(\infty)} - 1 \quad [11]$$

where $A(\infty)$ is the absorbance of an equilibrium sample.

Note that three measurements (e.g. $A^{ss}(1)$, $A^{ss}(2)$ and $A(\infty)$) are needed to extract the rate constants k_1' and k_2 .

Comparison of the predicted and measured transient responses is shown in Fig. 4 for typical student data.

CONCLUSIONS

THE ATTITUDE OF the students to the sequence of reactor experiments was substantially improved through use of the alkaline fading reaction. Some of the poorer students had conceptual difficulty with the reversible nature of the phenolphthalein reaction, and care had to be taken that they not only made all necessary measurements but also were on the right track in developing a kinetic model to represent the experiment. Even some better students made the common error of assuming ($[\text{Ph}^-] + [\text{PhOH}^-]$) constant in the transient CSTR experiment, i.e. confusing batch and flow behavior.

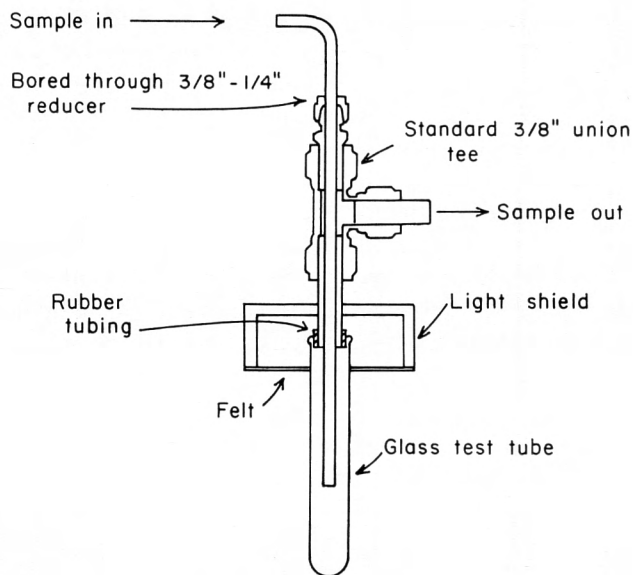
The visual nature of this reaction as carried out in clear glass reactors added considerably to the interest and gave tangible reinforcement of concepts that raw data often lacks. This allows misconceptions or blunders to be more easily uncovered. Some examples: the reversible nature of the reaction is obvious since the color never fades

completely; it is evident that the final color darkens with increasing temperature so the reaction must be exothermic; in the CSTR experiment the steady-state concentrations are noticeably different in the tanks and the distinction between equilibrium and steady state is seen; the moment of initiation can be established visually; and accidental contamination due to careless cleaning is immediately evident.

As the major objective of these experiments is to emphasize reactor properties rather than reaction properties, perhaps one of the simpler irreversible reactions should be used. On the whole, however, we feel that the new insights brought about through use of the more complex kinetics outweigh the drawbacks of a more involved experiment and analysis.

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Schematic of flow cell.

FIGURE 5.