filtrates & residues

Kinetics of the Fading of Phenolphthalein in Alkaline Solution

Lois Nicholson
West Springfield High School, Fairfax County, VA 22152

Phenolphthalein is used in several diverse applications. Chemistry students may be aware that phenolphthalein is an active ingredient in some laxatives, but they most frequently encounter phenolphthalein as an acid–base indicator to determine the equivalence point in a titration. If excess base is present in the flask at the end of the titration, the student may note that the pink color of phenolphthalein fades if the mixture stands for a while. But this slow fading is of no consequence to the titration, and the solution is discarded without further thought. Yet this fading of phenolphthalein in alkaline solution is interesting in its own right and can serve as the basis for an experiment illustrating pseudo-first-order kinetics. The procedure is extremely simple and foolproof, uses common reagents and equipment, and gives excellent results.

Structural Forms of Phenolphthalein

Although phenolphthalein is one of the most common acid–base indicators, its chemistry is not that of a simple conjugate acid–base pair, HIn–In$^-$. The structures of the important forms of phenolphthalein are shown in Figure 1. Phenolphthalein is colorless at pH 8 and lower. This colorless form has structure **1**, abbreviated H$_2$P. As the pH rises from 8 to 10, both phenolic protons are removed with approximately equal ease and the lactone ring opens, producing the familiar red–pink form with structure **2**, abbreviated P^{2-}. At still higher pH, the pink color slowly fades, producing structure **3**, abbreviated POH^{3-}.[1] All color changes are reversible, and while the conversion of H$_2$P to P^{2-} is extremely rapid and essentially complete by the time the pH is as high as 11, the conversion of P^{2-} to POH^{3-} at higher pH is sufficiently slow that its rate may be easily measured. Since P^{2-} is intensely colored, this conversion of P^{2-} to POH^{3-} can be monitored by measuring changes in absorbance, or optical density, of an alkaline solution of phenolphthalein.

Determination of the Pseudo-Order in Phenolphthalein

The fading of phenolphthalein in basic solution can be represented by the reaction: P^{2-} + OH$^-$ → POH^{3-}, and the rate law can be expressed rate = k[OH$^-$]^m[P^{2-}]^n. However, our procedure uses strongly basic solutions containing only a trace of phenolphthalein, so the OH$^-$ concentration exceeds that of phenolphthalein by a factor of at least 10^4 in any mixture. Therefore, during each run, the OH$^-$ concentration remains essentially constant, and the rate law then becomes rate = k_1[P^{2-}]^n. In this new rate law, $k_1 = k$[OH$^-$]^m, and the

[1] Lalanne, J. R. *J. Chem. Educ.* **1971**, *48*, 266–268.
[2] Masood, A.; Shastri, N. K.; Krishna, B. *Chim. Anal.* **1970**, *52*, 1289–1295.
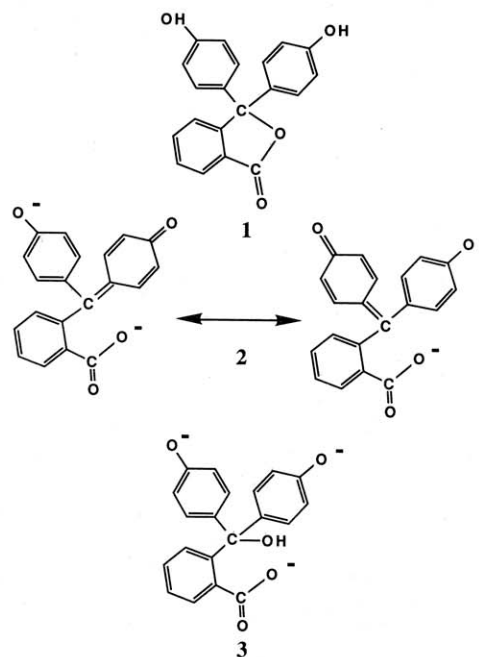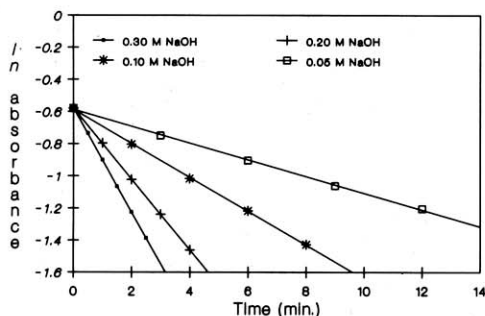

Figure 1. The structural forms of phenolphthalein.

reaction is said to be "pseudo nth order" in phenolphthalein (or in species P^{2-}). If the reaction is pseudo first order in phenolphthalein (or $n = 1$), a plot of ln [P^{2-}] versus time should give a straight line with slope equal to $-k_1$. According to Beer's law, the spectral absorbance of the solution is directly proportional to [P^{2-}], or [P^{2-}] = constant × (absorbance), so ln[P^{2-}] = ln (constant) + ln (absorbance). Therefore, a plot of ln (absorbance) versus time should also be a straight line with slope of $-k_1$, if the reaction is pseudo first order in phenolphthalein.

Experimental

Solutions and Equipment

NaOH solutions in the range 0.05–0.30 M give convenient rates of fading of phenolphthalein. For a particular concentration of NaOH, the rate of fading of phenolphthalein increases with increasing ionic strength.[2] This dependence of rate on ionic strength can be explained by the fact that the reaction involves the approach of two negatively charged ions, and their mutual repulsion is decreased in

Figure 2. Ln (absorbance) versus time, each at constant $[OH^-]$. In all graphs, the points are data, and each line is drawn using least-squares analysis.
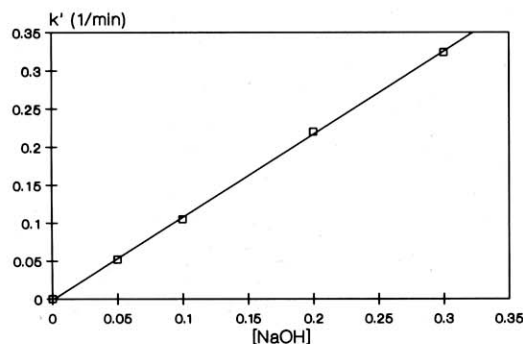

Figure 4. Plot of ln k_1 versus ln $[OH^-]$.

Figure 3. Plot of the pseudo-first-order rate constants, k_1, versus OH^- concentration.

an environment containing inert ions. In order to maintain constant ionic strength, standard 0.30 M NaOH and 0.30 M NaCl solutions are made, and a series of less concentrated NaOH solutions is prepared by diluting the standard NaOH with the NaCl solution. Since phenolphthalein is so intensely colored, in order to give solutions of reasonable absorbance, a 1% alcoholic phenolphthalein solution (commonly available as an acid–base indicator) is diluted further with ethyl alcohol, using four or five parts by volume alcohol for one part of 1% alcoholic phenolphthalein solution. The exact proportion in this dilution is not critical. The absorbance of solutions as a function of time is measured in a Spectronic 20 spectrophotometer at 550 nm. Times may be measured with an ordinary lab timer or a digital wrist watch.

Procedure

One drop of diluted phenolphthalein solution is added to about half a cuvette of NaOH solution, the cuvette is inverted several times to mix, and the absorbance is measured in the spectrophotometer at regular intervals of time. The exact volumes of NaOH and phenolphthalein solutions are not critical, and the exact time of mixing is not important. The decolorization of phenolphthalein is quite rapid in a 0.30 M NaOH solution, and absorbance readings should be taken every half minute. In 0.05 M NaOH the fading is relatively slow, and readings need be taken only every 2 or 3 min. Temperature changes can affect the rate of a reaction, so it is important that all solutions be at the same temperature. Since the temperature of a solution may increase in the light beam of the
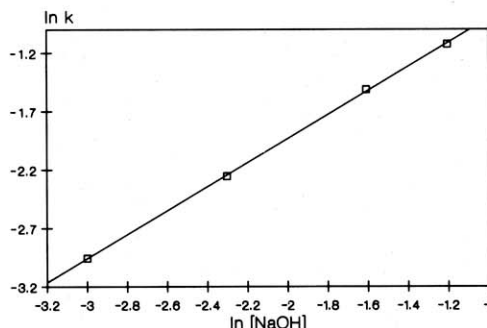
spectrophotometer, it is advisable to remove the cuvette from the spectrophotometer except when actually measuring absorbance.

Results

As shown in Figure 2, a plot of ln (absorbance) versus time gives an excellent straight line for any given NaOH concentration, indicating that the reaction is indeed first order in phenolphthalein. (After several half lives, especially in the more dilute NaOH solutions, the slope may begin to decrease due to the fact that the reaction approaches equilibrium as time passes.) The pseudo-first-order rate constant, k_1, for each NaOH concentration, is determined from the slope of each graph.

Determination of Order in Hydroxide

When the pseudo-first-order rate constants, k_1, are plotted versus the OH^- concentration, a straight line is obtained, as shown in Figure 3. Since $k_1 = k[OH^-]^m$, this straight line indicates that $m = 1$, that the reaction is also first order in OH^-. The slope of this latter plot gives the overall second-order rate constant, k, which is found from this procedure to have the value 1.1 L/mol-min at 23 °C and ionic strength of 0.30.

Another approach to determining the order in hydroxide ion is a ln–ln plot. Since $\ln k_1 = \ln k + m \ln[OH^-]$, the slope of the plot of ln k_1 versus ln $[OH^-]$ should equal m, the order with respect to OH^-. Figure 4 shows this plot, and m determined in this manner has the value 1.03, further confirming that the reaction is first order in OH^-.

Conclusion

It is especially instructive for students to understand which measurements are not particularly critical in this procedure and what must be done carefully, and why. Not critical are the exact concentration of phenolphthalein, the time of mixing, and the duration of the experiment as long as a few time intervals are measured. More critical are the dilutions of the series of NaOH solutions with care taken to maintain constant ionic strength, and the measurement of exact time *intervals*. This simple experiment enhances students' understanding of important concepts of chemical kinetics and gives reliable results, using common reagents and equipment. And it shows yet another use for phenolphthalein!