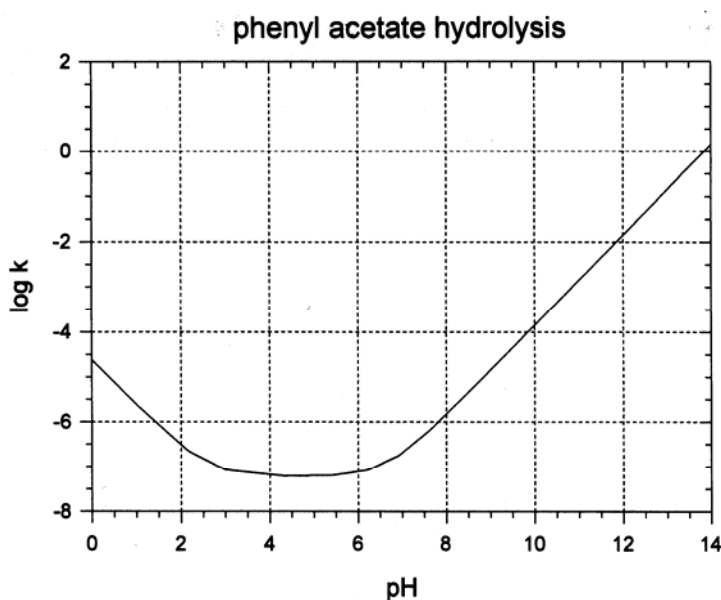
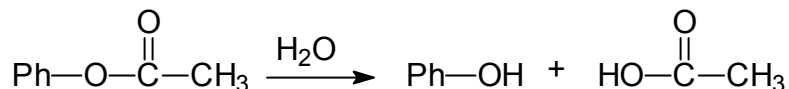


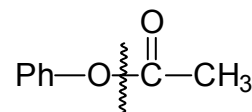
pH rate profiles

Before starting a discussion of acid and base catalysis it is perhaps helpful to mention a useful way of representing acid base behavior. A pH-rate profile is a plot of $\log k_{\text{obs}}$ (for acid - base - neutral reaction) vs pH. For most cases buffers will have been used to control pH, but to construct a pH rate profile one should extrapolate to zero buffer for each pH to remove the effects of buffer.

An example: Phenyl acetate hydrolysis



For the pH meter accessible region (\sim pH 1 to 13) there are three reaction paths leading to hydrolysis of phenyl acetate. All go by way of acyl oxygen cleavage,



and are not distinguished by their products. For this pH range the rate law is

$$\text{Rate} = d[\text{P}]/dt =$$

$$k_0[\text{PA}] + k_A[\text{H}^+][\text{PA}] + k_B[\text{OH}^-][\text{PA}]$$

Which leads to pseudofirst order behavior at any particular pH. The pseudofirst order rate constant is given by:

$$-d[\text{PA}]/dt = k_{\text{obs}}[\text{PA}]$$

$$k_{\text{obs}} = k_0 + k_A[\text{H}^+] + k_B[\text{OH}^-]$$

The values of the rate constants are:

$$k_0 = 6.03 \times 10^{-8} \text{ s}^{-1}$$

$$k_A = 2.34 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_B = 1.43 \text{ M}^{-1} \text{ s}^{-1}$$

A pH rate profile is a plot of $\log k_{\text{obs}}$ vs pH (One sometimes sees plots of k_{obs} vs pH but this is much less useful: one cannot by inspection tell if simple acid or base catalysis has been reached. This is easy for a plot of $\log k_{\text{obs}}$ vs pH, since simple acid catalysis gives a region of slope -1, and simple base catalysis gives a slope of +1)

The slope of a plot of $\log k$ vs $\log [H^+]$ at a given pH gives the order in $[H^+]$ relative to the major form of the starting material at that pH; this is in principle a general method, but is rarely used for other possible reactants because of the difficulty in using a wide enough range of concentrations to give good variation in $\log [X]$.

For our example the following approximations can be made, simplifying the overall equation (recall that $K_w = [H^+][OH^-]$ and thus $[OH^-] = K_w/[H^+]$)

$$k_{\text{obs}} = k_o + k_A[H^+] + k_B[OH^-]$$

At high enough $[H^+]$ (low enough $[OH^-]$) the full expression for k_{obs} must simplify to

$$k_{\text{obs}} \approx k_A[H^+]$$

Then $\log(k_{\text{obs}}) = \log k_A + \log([H^+]) = \log k_A + \text{pH}$

and the slope of the pH rate profile is -1. Also at $\text{pH} = 0$, $\log(k_{\text{obs}}) = \log k_A$

At low enough $[H^+]$ (high enough $[OH^-]$) the full expression for k_{obs} must simplify to

$$k_{\text{obs}} \approx k_B[OH^-]$$

Then $\log(k_{\text{obs}}) = \log(k_B) + \log([OH^-])$

Since $K_w = [H^+][OH^-]$, $\log(K_w) = \log([H^+]) + \log([OH^-])$

and $\log([OH^-]) = \log(K_w) - \log([H^+])$

Thus $\log(k_{\text{obs}}) = \log(k_B) + \log(K_w) - \log([H^+]) = \log(k_B) + \log(K_w) + \text{pH}$

and the slope of the pH rate profile is +1.

Also at $\text{pH} = 14$, $\log(k_{\text{obs}}) = \log(k_B) - 14 + 14 = \log(k_B)$

We are interested in the slopes for each section of the pH rate profile because that tells the kinetic order in the corresponding part of the rate law and thus the number of charges in the transition state for the corresponding mechanism

If the slope of a pH rate profile is zero, then the transition state has the same number of protons as the major form of the starting material for this pH range.

If the slope of a pH rate profile is 1 (slope of $\log k$ vs $\log[H^+]$ is -1) then the transition state has one fewer protons than the major form of the starting material for this pH range.

If the slope of a pH rate profile is -1 (slope of $\log k$ vs $\log[H^+]$ is 1) then the transition state has one more protons than the major form of the starting material for this pH range.

It is perhaps easiest to understand pH rate profiles by looking separately at parts of the curve, and working out a mechanism consistent with the facts for each region. In doing so we bear in mind that kinetics tells us the composition of the transition state. In the particular case of a pH rate profile, the slope of the plot in a particular region tells us the proton composition of the transition state relative to the major species of starting material in that pH region.

For most cases where we analyze experimental data, the line of best fit is the thing of interest and the slope is what we are trying to determine. For pH rate profiles we have strong reasons to expect integer slopes and what is of interest are the limiting lines which describe the profile; the intercepts lead to the rate constants.

For a pH rate profile we analyze the plot into regions with or approaching a limiting slope of 0, ± 1 , or occasionally ± 2 .

For our example, the hydrolysis of phenyl acetate, the following approximations can be made:

below pH 4

$$k_{\text{obs}} = k_0 + k_A[\text{H}^+]$$

below pH 1

$$k_{\text{obs}} = k_A[\text{H}^+]$$

between pH 4 and 5

$$k_{\text{obs}} = k_0$$

above pH 5

$$k_{\text{obs}} = k_0 + k_B[\text{OH}^-]$$

above pH 8

$$k_{\text{obs}} = k_B[\text{OH}^-]$$

Acid range: The profile curls up around pH 3, and looks like a straight line from pH 2 to 1. This marks “cutting in and taking over” introduction and increasing importance of the acid catalyzed mechanism. $k_A = 2.34 \times 10^{-5} \text{M}^{-1} \text{s}^{-1}$. In the left side (pH 1-2) region the important reaction is the acid catalysis. At some point as one goes from neutral to acid medium

$$k_A[\text{H}_3\text{O}^+] = k_0$$

This happens when

$$[\text{H}_3\text{O}^+] = k_0/k_A = 6.03 \times 10^{-8} \text{s}^{-1} / 2.34 \times 10^{-5} \text{M}^{-1} \text{s}^{-1} = 2.58 \times 10^{-3} \text{M}$$

or pH = 2.59

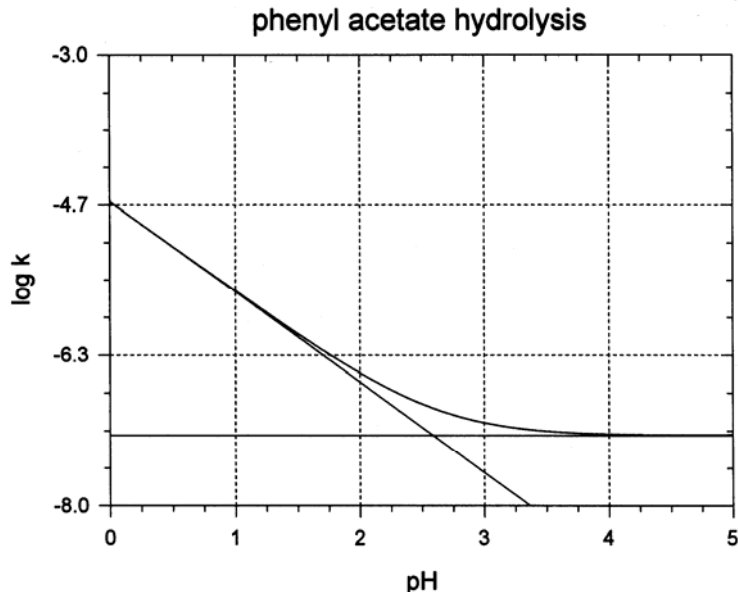
Above pH 2.59, $k_0 > k_A[\text{H}_3\text{O}^+]$

Below pH 2.59, $k_A[\text{H}_3\text{O}^+] > k_0$

At pH 2.59 the two contributions are equal, i.e.

$$\begin{aligned} k_0 &= k_A[\text{H}_3\text{O}^+] = k_A(10^{-2.59}) \\ \log k_{\text{obs}} &= \log(k_0 + k_A[\text{H}_3\text{O}^+]) = \log(2 k_0) \\ &= \log k_0 + \log(2) = \log k_0 + 0.301 \end{aligned}$$

Thus a pH rate profile always has rounded



corners

Only when the pH is more than one log unit away from the crossover point can we neglect the slower process. (It will be less than 10% of k_{obs}). At pH 3.59 (2.59 - 1) or 1.59 (2.59 + 1) the slower term will be 10% of the larger term. From the crossover calculation, $k_o = k_A(10^{-2.59})$

$$\text{At pH } 3.59, k_{\text{obs}} = k_o + k_A[\text{H}^+] = k_A(10^{-2.59}) + k_A(10^{-3.59}) = k_o + 0.1k_o = 1.1k_o$$

$$\begin{aligned} \text{At pH } 1.59, k_{\text{obs}} &= k_o + k_A[\text{H}^+] = k_A(10^{-2.59}) + k_A(10^{-1.59}) \\ &= 0.1k_A(10^{-1.59}) + k_A(10^{-1.59}) = 1.1k_A(10^{-1.59}) \end{aligned}$$

In the acid range

$$k_{\text{obs}} = k_A[\text{H}_3\text{O}^+]$$

or, taking logs

$$\begin{aligned} \log k_{\text{obs}} &= \log k_A + \log [\text{H}_3\text{O}^+] \\ &= \log k_A - \text{pH} \end{aligned}$$

Thus a plot of $\log k_{\text{obs}}$ vs pH yields a straight line of slope -1 and intercept (at pH = 0) of $\log k_A$.

(Note the |slope| is 1 because the reaction is first order in $[\text{H}_3\text{O}^+]$. For a reaction with the rate law $k_{\text{obs}} = k_A[\text{H}_3\text{O}^+]^2$, $\log k_{\text{obs}} = \log k_A - 2\text{pH}$ and |slope| = 2

For an acid catalyzed reaction the slope of a plot of $\log k_{\text{obs}}$ vs $\log [\text{H}^+]$ is +1, whiel for a plot of $\log k_{\text{obs}}$ vs pH it is -1.

$$\text{Note that the intercept, i.e. } \log k_{\text{obs}} \text{ at pH} = 0 \text{ is } \log k_A = -4.6 = \log (2.34 \times 10^{-5})$$

In the basic range (pH > 8) clearly a straight line of slope 1

In the transition from uncatalyzed to base catalyzed reaction there is a crossover between pH 5 and 8. The crossover happens when

$$k_o = k_B[\text{OH}^-]$$

$$\text{ie at } [\text{OH}^-] = k_o/k_B = 6.03 \times 10^{-8} / 1.43 = 4.22 \times 10^{-8}$$

or $\text{pOH} = 7.37$

or $\text{pH} = 14 - 7.37 = 6.62$

$$k_{\text{obs}} = k_{\text{B}}[\text{OH}^-]$$

$$\begin{aligned} \log k_{\text{obs}} &= \log k_{\text{B}} + \log [\text{OH}^-] \\ &= \log k_{\text{B}} + \log K_{\text{w}} - \log [\text{H}_3\text{O}^+] \\ &= \log k_{\text{B}} + \log K_{\text{w}} + \text{pH} \end{aligned}$$

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Again $\log k_{\text{obs}}$ vs pH yields a straight line, this time with slope = +1, and intercept at $\text{pH} = 14$ of $\log k_{\text{B}}$.

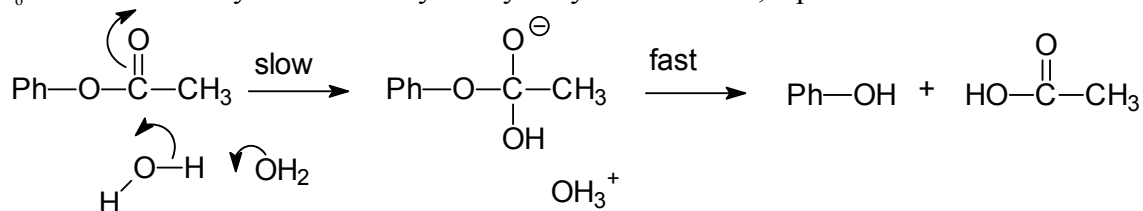
$$k_{\text{B}} = 1.43\text{M}^{-1}\text{s}^{-1}; \log k_{\text{B}} = 0.155$$

Mechanisms

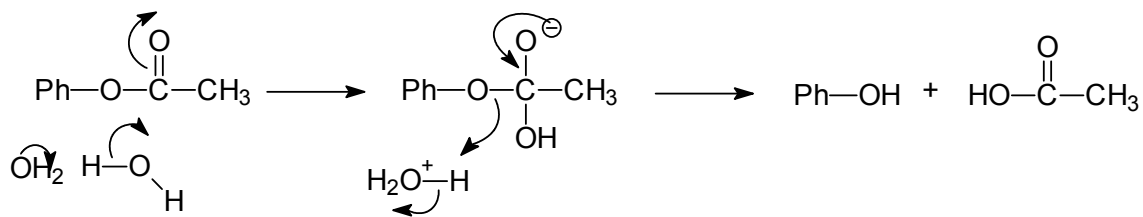
k_0 (uncat) First we look at the midrange: the plot is flat, i.e. a straight line of slope zero.

$$k_{\text{obs}} = k_0 = 6.03 \times 10^{-8} \text{s}^{-1}$$

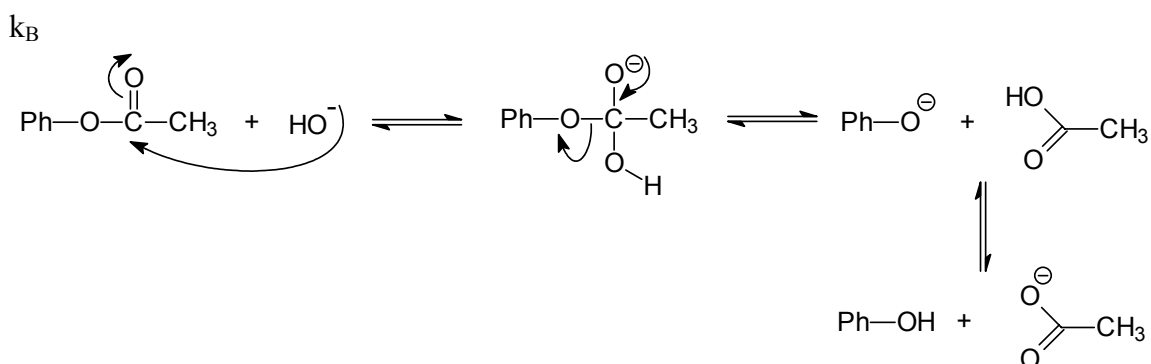
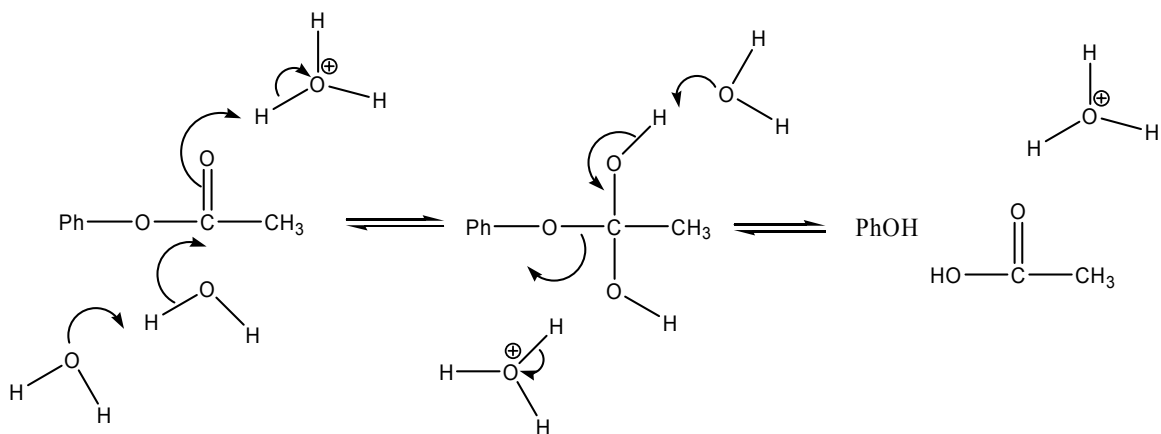
k_0 refers to the very slow uncatalyzed hydrolysis of PhOAc; a plausible mechanism is:



Phenoxide is a better leaving group than hydroxide so it is possible that the second step is simply unimolecular breakdown of the anion tetrahedral intermediate, or it may be catalyzed by H_3O^+ in a fashion analogous to the microscopic reverse of the first step.

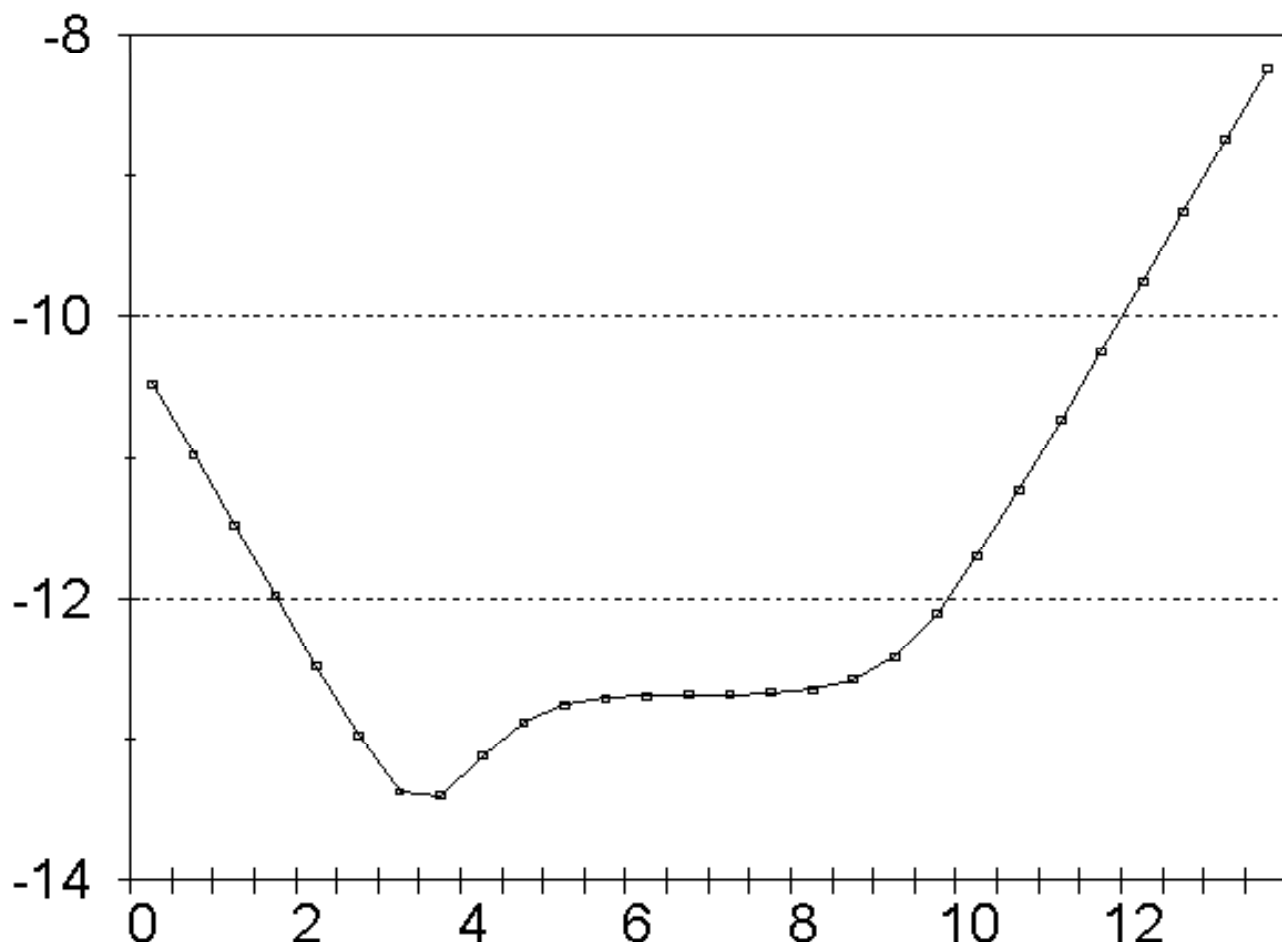


k_{A}



Although it is rare it is possible for a pH rate profile to have a slope of -2 or +2. One example is the hydroxide catalyzed hydrolysis of N-methyl-N-(p-nitrophenyl)trifluoroacetamide, where the slope of the pH rate profile at high pH is +2. This means that the transition state has two fewer protons than the major form of the starting material for this pH range. This in turn means that the reaction proceeds by way of the dianionic tetrahedral intermediate, which is able to drive out the N-methyl-p-nitroanilide ion.

The second thing which can affect a pH rate profile is a titration of a reactant, converting it into a more (or less) reactive form. This will lead to a curve of the form of the titrations generally superimposed upon a pH-rate profile of the form discussed above. An example is the exchange of CD_3COOH in H_2O (a reaction run at 100-200°C; the rate constants can be extrapolated to room temperature). Although most of these reactions are too slow to be of much use, the exchange of acetate at 100°C with hydroxide is a practical process.



The profile shows an acid catalyzed path, involving H^+ and CD_3COOH , a base catalyzed path, involving OH^- and CD_3COO^- , and a titration of CD_3COOH to CD_3COO^- . It should be noted that there is a mechanistic ambiguity about the titration curve, since the important species could be H_2O and CD_3COO^- or OH^- and CD_3COOH ; these combinations are kinetically indistinguishable, since they have the same overall composition; chemical intuition allows us to decide.

The rate constants which can be extracted from these data are:

For CH_3COOH :	$k_{H^+} = 5.7 \times 10^{-11} M^{-1} s^{-1}$
	$k_{OH^-} = 3.8 \times 10^{-5} M^{-1} s^{-1}$
for CH_3COO^- :	$k_{H_2O} = 1.1 \times 10^{-13} s^{-1}$
	$k_{OH^-} = 3.1 \times 10^{-9} M^{-1} s^{-1}$

Another example which shows the effect of titration of a reactant involves hydrolysis of acetyl imidazole. The protonated acetyl imidazole (acetyl imidazolium ion) reacts more rapidly with water than neutral acetyl imidazole. Hydroxide reacts more rapidly than water with acetyl imidazole.

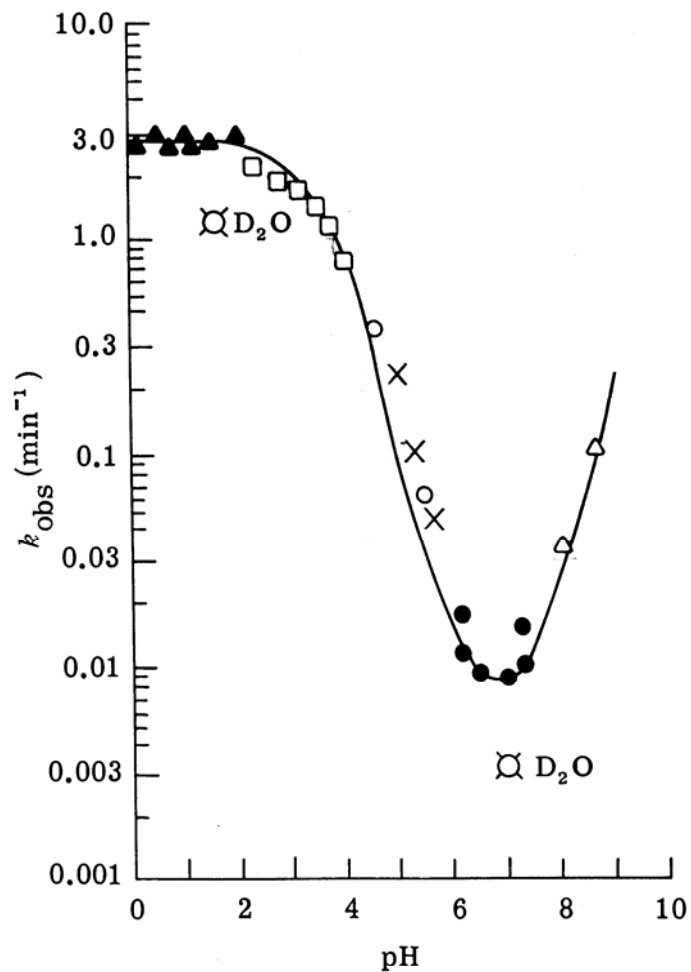


Fig. 1-14 Logarithmic plot of the rate of *N*-acetylimidazole hydrolysis, extrapolate to buffer concentration, against pH at 25.0° and 0.2 ionic strength. (Ref. 26.)

