

Extreme Ester Hydrolysis

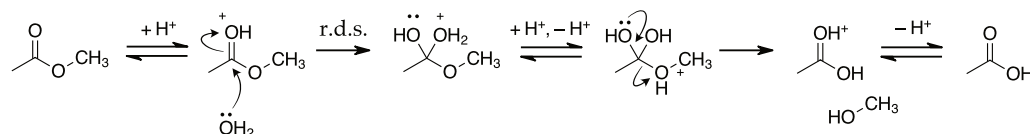
Barry Linkletter

This exploration consider acid-catalyzed hydrolysis of esters in extreme acid conditions.

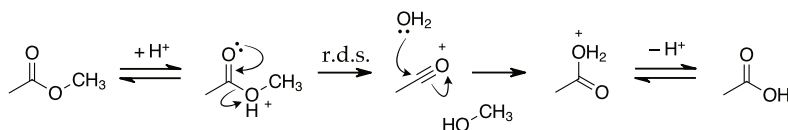
Possible Mechanisms for Hydrolysis

Let us consider the possible mechanisms for hydrolysis of esters in extreme acid media. We will be using data from a Canadian contribution that reports rates of ester hydrolysis in mixtures of sulphuric acid and water.¹

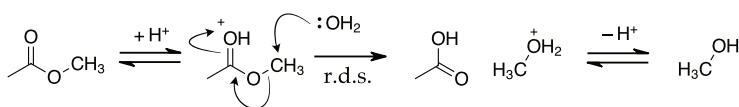
Ester hydrolysis in acid can occur via an acid-catalyzed mechanism that involves activation of the carbonyl group by equilibrium protonation, followed by a rate-determining addition reaction. This is designated as an A_{Ac}2 mechanism. However, in some cases, there are other observed mechanisms.



If the substituent on the carbonyl group can stabilize a carbocation then it is possible that the fastest route to hydrolysis would be via the unimolecular departure of the protonated alcohol group. This is designated as an A_{Ac}1 mechanism. The acylium ion intermediate is generally only observed when the substituent is stabilizing and the conditions have minimal nucleophiles present. Mixtures that are mostly H₂SO₄ will have very little free water available to act as a nucleophile. Perhaps we will see this mechanism become important in extreme acid mixtures.



If the nucleophile cannot attack the carbonyl group for some reason (e.g. sterics) then we may see the hydrolysis occur via an S_N2 substitution reaction at the carbon of the alcohol group. This is designated as an A_{Al}2 mechanism.



This document was produced using the L^AT_EX typesetting language with the Tufte-handout document class. Chemical diagrams were created in ChemDoodle and calculations and plotting were performed using Python tools in a Jupyter Notebook. Diagrams and plots were further edited in Affinity Designer

¹ "Mechanisms of ester hydrolysis in aqueous sulfuric acids." K. Yates, R.A. McClelland, *J. Am. Chem. Soc.*, 1967, 89, 2686-2692. <https://doi.org/10.1021/ja00987a033>

Figure 1: Acid-catalyzed hydrolysis of an ester via a bimolecular acyl substitution reaction (A_{Ac}2). ↑

Figure 2: Acid-catalyzed hydrolysis of an ester via a unimolecular departure of the leaving group (A_{Ac}1). ←

Figure 3: Acid-catalyzed hydrolysis of an ester via nucleophilic attack at the carbon of the alcohol group (A_{Al}2). ←

If the carbon of the alcohol group in the ester can bear a positive charge easily then we may see a unimolecular dissociation of the acid group from that carbon to give a carbocation. The *t*-butyl group is a classic example and it has a famous abbreviation – Boc. Other carbon groups may also result in this mechanism becoming predominant in minimally nucleophilic conditions such as extreme acid mixtures. This is an example of an $A_{Al}1$ mechanism.

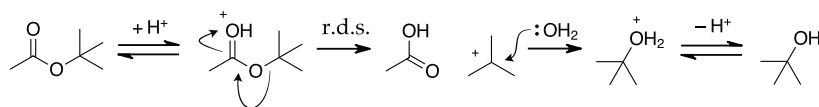
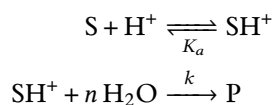


Figure 4: Acid-catalyzed hydrolysis of an ester via dissociation of the carbon of the alcohol group ($A_{Al}1$).

The A_{Ac} and A_{Al} mechanisms can be distinguished by isotopic labeling of water, by secondary kinetic isotope effects or by observing the stereochemistry of the alcohol product. The unimolecular and bimolecular mechanisms can be distinguished by observing a rate dependence on the activity of water. The Yates paper¹ investigates the kinetics for hydrolysis of several esters in acid mixtures with a wide range of water activity. All four of the above reaction pathways are observed, depending on the ester and the reaction conditions.

The $A_{Ac}2$ Mechanism

On examination of the $A_{Ac}2$ mechanism presented in figure 1 above, we can establish the reaction scheme and rate law.



Scheme 1: Reaction scheme for the $A_{Ac}2$ mechanism. 'S' is the ester substrate for the reaction.

The rate law can be expressed as shown in eq. 1 below. Take note of the stoichiometry term, n , for water. Yates et al. were investigating the possibility of a higher-order dependence on $[H_2O]$ in highly acidic media. In dilute water it is impossible to determine how many waters are involved in the transition state for the rate-determining addition step. This is unimportant as the concentration of water in dilute solution does not change and it is folded into the pseudo-first order rate constant for the reaction. But what if the concentration of water was actually changing?

$$\frac{\partial P}{\partial t} = k \frac{[H^+]}{K_a + [H^+]} [H_2O]^n \cdot [S]_t \quad (1)$$

The pseudo-first order rate constant can be defined as...

$$k_{obs} = k \frac{[H^+]}{K_a + [H^+]} [H_2O]^n \text{ where } \frac{\partial [P]}{\partial t} = k_{obs} \cdot [S]_t \quad (2)$$

Of course, we are well beyond a dilute solution where ideal behaviour of ions is assumed. We should use the activities of acid and water, not their actual concentrations. The activity of acid can be expressed using an acidity function such as H_0 .

$$H_0 = -\log h_0 \quad (3)$$

h_0 is the activity of the acidic medium for transferring a proton to the aniline nitrogen of an indicator dye. The aniline system behaves differently than an ester for protonation. Due to their reactivity, there have been no acidity functions for ester substrates reported. The authors measured the protonation of some unreactive esters in high concentrations of H_2SO_4 and determined an acidity function for esters, $H_S = 0.62H_0$. They made the assumption that this relationship would hold true across the range of H_2SO_4 mixtures used. The fact that other acidity functions such as H_R show a linear proportionality with H_0 backs up this assumption. I plotted literature data sets for H_0 and H_R in figure 5. Do you agree?

The activity of water, a_{H_2O} in various mixtures with H_2SO_4 can be measured. Tables for a_{H_2O} are available in the literature.² We can now state k_{obs} in terms of h_0 and a_{H_2O} ...

$$k_{obs} = k \frac{h_0^m}{K_a^m + h_0^m} a_{H_2O}^n, \text{ where } m = 0.62 \quad (4)$$

We can now construct a log-log plot of the form...³

$$\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m} = n \log a_{H_2O} + \log k \quad (5)$$

Reaction Kinetics for Methyl Acetate

The rate data for methyl acetate (and several other esters) in mixtures of sulphuric acid is provided in the paper. The data is listed in table 1 and the plots of k_{obs} vs. % H_2SO_4 and mole fraction H_2SO_4 ($X_{H_2SO_4}$) are presented in figure 2.

The lines in the plots are smoothed interpolations and do not represent any mathematical model. Observe that the rate increases as the amount of sulphuric acid in the mixture increases. However, as the acid content increases the rate eventually starts dropping. Examination of the rate law for the $A_{Ac}2$ reaction shows that the rate is dependant on both acidity and the amount of water available to act as a nucleophile. The red dashed line on the plots is the mole fraction of water, X_{H_2O} . We see that the concentration of water diminishes in stronger acid mixtures, however this reduction in concentration is not enough to explain the drop in rate. What is really dropping is the activity of the water, a_{H_2O} , shown in the gray dashed line. The a_{H_2O} is the apparent mole fraction of water in the mixture. It drops rapidly as we increase the amount of acid because hydronium ion is not a nucleophile.⁴

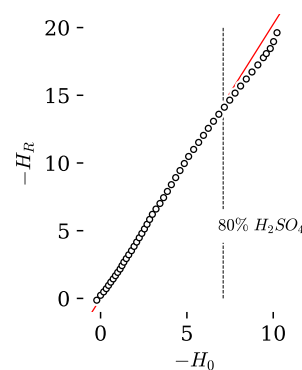


Figure 5: A plot of H_R vs. H_0 . ↑

It is a linear trend, although imperfect. We observe that $H_R \approx 1.95H_0$ in the range of 4 to 80%. Compare with figure 2 in the Yates paper¹ The *Python* notebook for this plot can accessed via Google Colab at https://colab.research.google.com/github/blinker/4410PythonNotebooks/blob/main/Class_30/Yates-Fig5-HRH0.ipynb

² "The Thermodynamic Properties of Aqueous Sulfuric Acid Solutions and Hydrates from 15 to 300 K." W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin *J. Am. Chem. Soc.*, 1960, 82, 62-70 <https://doi.org/10.1021/ja01486a014>

³ The authors assume that $h_0 \ll K_a$ and so the plot will collapse to the form presented in the paper...

$$\log k_{obs} + mH_0 = n \log a_{H_2O} + (mpK_a + \log k)$$

$$\log k_{obs} + mH_0 = n \log a_{H_2O} + \text{const.}$$

The approach that I am using here is mentioned in footnote 21 of the paper.¹

⁴ Compare figure 6 above with figure 1 in the paper.¹ Note that the figure presented by Yates et al. shows a second mechanism becoming predominate at very high acidity. The data for these final few points is not included in Table 1 of their paper. This was likely a printing error. There was no erratum published so the authors obviously didn't feel that this omission was a big deal. We would not have used those final points anyway as they are the result of an alternate mechanism and do not represent the kinetics of the $A_{Ac}2$ pathway.

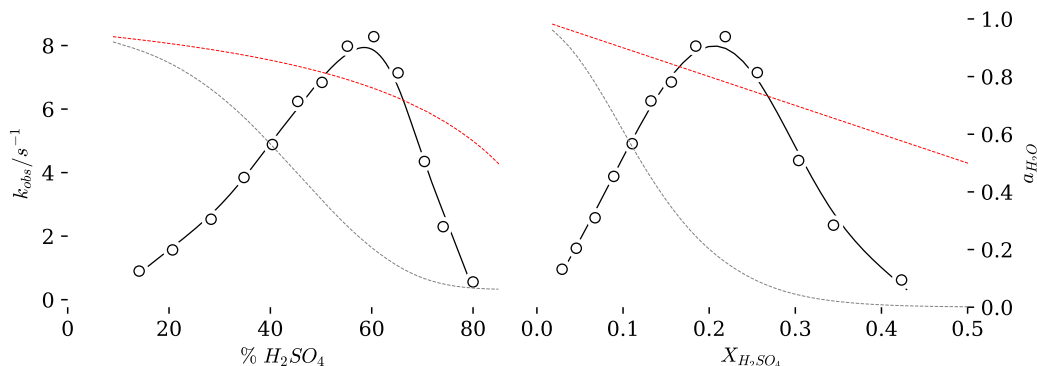


Figure 6: Plots of k_{obs} vs. $\%H_2SO_4$ and k_{obs} vs. mole fraction H_2SO_4 . ↑

The grey dashed line is the activity of water and the red dashed line is the mole fraction of water. Curves are B-spline interpolations of smoothed data. The *Python* notebook for this plot can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig6-MeOAc.ipynb

A Log-Log Plot

A log-log plot would be better for interpreting the rate vs. acidity. We will use the acidity function, $-H_S$, to represent the log of the activity of acid. We will plot $\log a_{H_2O}$ against $-H_S$ as presented in figure 7.

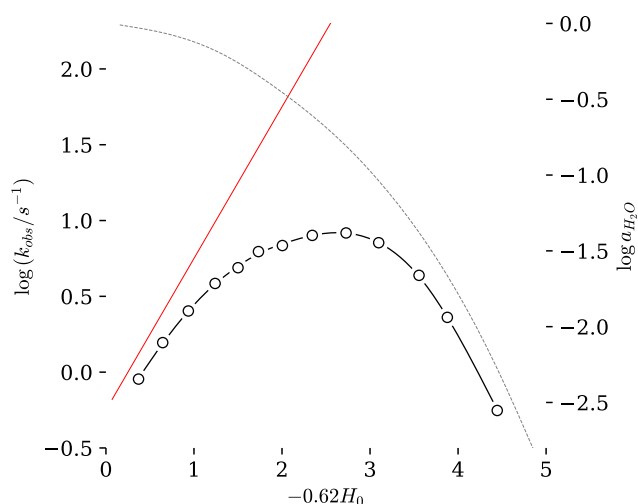


Figure 7: Log-log plot of k_{obs} and a_{H_2O} vs. H_S . The grey dashed line is $\log a_{H_2O}$ and the red line is a simple slope of 1.0, representing theoretical first-order dependence on the acidity of the mixture.

←
Curves are B-spline interpolations of smoothed data. The *Python* notebook for this plot can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig7-MeOAc.ipynb

According to the rate law, the log-log plot should have a slope of 1 in acidic conditions and then curve over to a slope of zero when the system is more acidic than the pK_a of the protonated ester and $[SH^+]$ approaches a maximum value. We do see that the slope of the curve seems to approach 1.0 as the solution becomes more dilute. However, we do not observe the rate reaching a constant value, rather it decreases sharply as the mole fraction of H_2SO_4 increases. As discussed above, this is because the value of k_{obs} is also dependant on the activity of water, a_{H_2O} .

Table 1: Pseudo-first order rate constants for hydrolysis of methyl acetate at 25 °C.¹ ↓

| $\%H_2SO_4$ | $k_{obs}/10^{-2} \text{ min}^{-1}$ |
|-------------|------------------------------------|
| 14.1 | 1.50 |
| 20.7 | 2.61 |
| 28.3 | 4.22 |
| 34.8 | 6.41 |
| 40.4 | 8.14 |
| 45.4 | 10.4 |
| 50.2 | 11.4 |
| 55.2 | 13.3 |
| 60.4 | 13.8 |
| 65.2 | 11.9 |
| 70.4 | 7.25 |
| 74.1 | 3.83 |
| 80.0 | 0.931 |

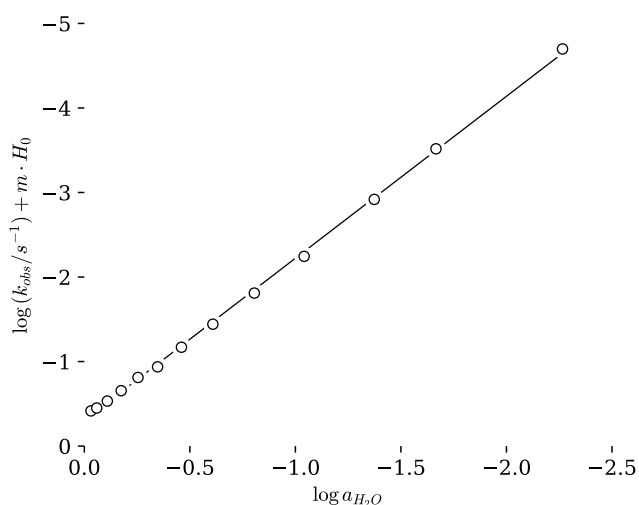
Plotting the Rate Law

The rate law established in equation 5 above would allow us to plot the rate (as dependant on H_S) against a_{H_2O} . We should obtain a straight line with a slope equal to the molecularity (reaction order) of water. Yates et al. were investigating the observation that these ester hydrolysis reactions involved multiple water molecules in the transition state of the r.d.s. and so we should be prepared to see the slope be greater than one.

However, we will first replicate the exact approach of the authors where they assume that the fraction of SH^+/s is minimal ($H_0 < pK_a$). The authors plotted the following relationship shown in equation 6 and the plot is presented in figure 8 below.

$$\log k_{obs} + mH_0 = n \log a_{H_2O} + const. \quad (6)$$

We observe the same results as reported by the authors: $n = 1.92$. We see from the rate law in equation 1 that n is the order in H_2O .



We would conclude that the rate-determining-step involves two molecules of water and this idea is discussed at length in the paper.¹ I challenge you to apply this plotting method to the other ester results presented in the paper and you should see the same results for the data describing the $A_{Ac}2$ mechanism. Compare your results to those reported in table II of the paper.

The *Python* notebook for the plots in Figures 8 and 9 below can accessed via Google Colab at <https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class.30/Yates-Fig8-rate.vs.aH2O.ipynb>

Figure 8: Plot of $\log k_{obs} + mH_0$ vs. $\log a_{H_2O}$. m is set to 0.62. Compare this plot to figure 3 of the paper.¹

The line equation is...

$$y = 1.92x - 0.31$$

$$r^2 = 0.999$$

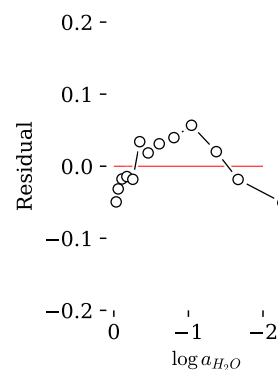


Figure 9: A plot of the residuals. ↑

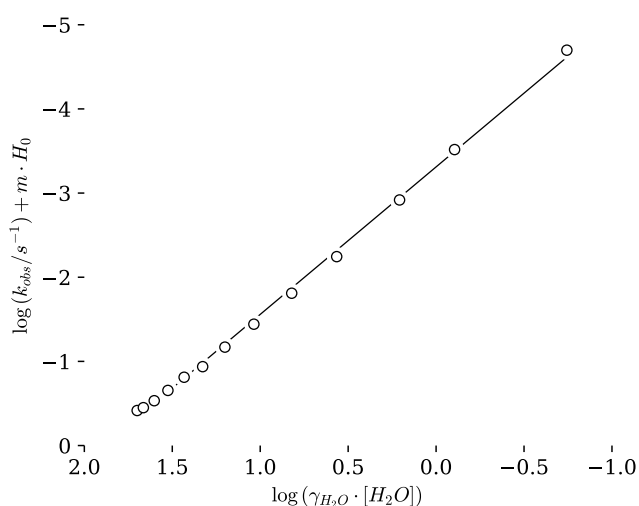
Comments and Criticisms

As always, I have some notes. Observe the plot of the residuals for figure 8 on the previous page presented in figure 9. The line fit is excellent ($r^2 = 0.999$) and the deviation from the line fit is small, but we observe a systematic pattern in the residual plot. We are not capturing the full system in our model.

The values of $a_{\text{H}_2\text{O}}$ used by the authors are clearly not in units of molar concentration. Upon examination of the data in the referenced publication,² we see that $a_{\text{H}_2\text{O}}$ is the “apparent mole fraction” of water in the mixture, $\gamma_{\text{H}_2\text{O}} \cdot X_{\text{H}_2\text{O}}$ and not the effective concentration of water, $\gamma_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]$.

We can calculate $\gamma_{\text{H}_2\text{O}}$ using the data table² of $a_{\text{H}_2\text{O}}$ vs. %H₂SO₄ and we can obtain [H₂O] vs. %H₂SO₄ from literature data tables.⁵

With a little effort we can convert $a_{\text{H}_2\text{O}}$ to $\gamma_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]$. Plotting the two sets of values against each other shows that they are similar as presented in figure 10 where we see a linear relationship with a slope near unity. So all this work won't change the result much, but it will make it more defensible.



Again we get a great correlation but still see the systematic variation in the residuals that indicates an incomplete model.

Including the K_a Value

The authors used a rate law that assumed the magnitude of the acidity was well below the pK_a ($H_0 < pK_a$). This is almost true, but in the data we will see that H_0 is approaching the value of pK_a and, for some of the data points, there could be deviation from the model.

To account for this we should plot the full rate law as described in equation 5 on page 3. We will need a value for the pK_a of the SH^+ species (the

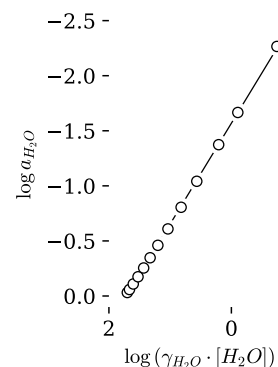


Figure 10: A log-log plot of $a_{\text{H}_2\text{O}}$ vs. $\gamma_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]$. ↑ The line equation is...

$$y = 0.92x - 1.57$$

$$r^2 = 0.9998$$

⁵ "CRC Handbook of Chemistry and Physics." Many copies are available in the library stacks (QD65.H3) and there is an [online version available](#). A data table that lists the [densities of mixtures of sulfuric acid](#) can be found on page 9-84 of the 2025 edition.

Figure 11: Plot of $\log k_{obs} + mH_0$ vs. $\gamma_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]$.

← The line equation is...

$$y = 1.75x - 0.33$$

$$r^2 = 0.998$$

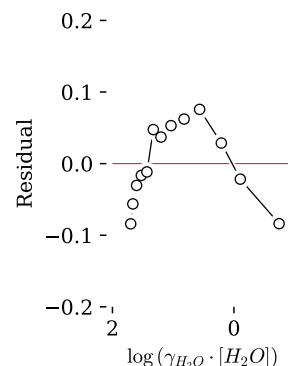


Figure 12: A plot of the residuals. ↑

The *Python* notebook for the plots in Figures 10, 11 and 12 above can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig10-rates_vs_gammaH2O.ipynb

protonated ester). The authors quote a value of -7.2 and that is what we will use for now.⁶ The authors also defined the H_S scale as $H_S = m \cdot H_0$ and measured the value of m to be 0.62 based on spectroscopic observations of ester protonation.¹ Based on these parameters we can create a model for the rate law from equation 5 (reproduced below, with the values of m and K_a stated.)

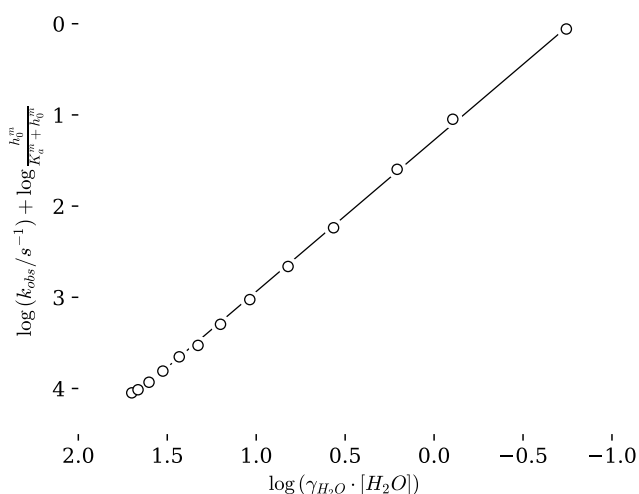
$$\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m} = n \log a_{H_2O} + \log k$$

$$m = 0.62$$

$$K_a = 10^{7.2}$$

$$a_{H_2O} = \gamma_{H_2O} \cdot [H_2O]$$

Let us plot $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ as presented in figure 13 using the values for m and pK_a selected by Yates et al.



Again we have a plot with an amazing correlation coefficient and a set of residuals that follows the line fit closely. There still seems to be structure to the residual plot that is beyond random variation but it is now much less pronounced. The slope is about 1.7 , which still is indicative of more than one water molecule being involved in the r.d.s. We shall soon see that the slope is very sensitive to the value of m that we choose. This may also be due to a lack of an accurate acidity function for ester protonation in extreme acid conditions. Recall that the authors ball-parked their tentative H_S scale by setting it as a fraction of H_0 ($H_S = 0.62H_0$).

⁶ “The possibility of a cyclic mechanism for acid-catalyzed ester hydrolysis.” C.A. Lane, M.F. Cheung, and G.F. Dorsey, *J. Am. Chem. Soc.*, **1968**, *90*, 6492-6494. <https://doi.org/10.1021/ja01025a046>

Figure 13: Plot of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ where $m = 0.62$ and $pK_a = -7.2$.

The line equation is...

$$y = 1.66x + 1.28$$

$$r^2 = 0.999$$

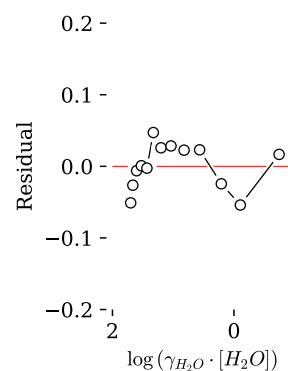


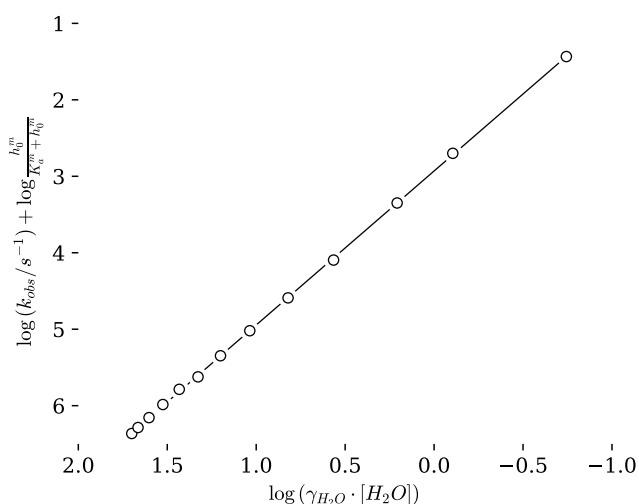
Figure 14: A plot of the residuals. ↑

The *Python* notebook for the plots in Figures 13 and 14 above can accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig13-rate_vs_gammaH2O.ipynb

Optimizing the Values for m and pK_a

We now know that the line fit is dependant on the set values of m and pK_a . Changing these constants will change the values on the Y-axis and affect the slope and the quality of the fit. So far, our line fits have been fantastic no matter what we do. Will that hold up if we tweak the constants that define the behaviour of the ester acid equilibrium?

I will survey a series of values for m and pK_a and determine the value of the Pearson correlation constant, r^2 for the line fit of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ in each case. Figure 15 shows a contour plot that explores the surface for r^2 w.r.t. these two constants. Optimizing for the fit gives a values of $m = 0.72$ and $pK_a = -9.5$.



We see a slope of almost exactly 2 when using those parameters. This seems to solidly confirm that the order in $[H_2O]$ is 2. It seems too good to be true. Is it? The optimized value of pK_a is two orders of magnitude from the observed value. That gives me pause.

The Other Optimum

Observe in figure 15 that there is a second slight dip in the surface for $r^2 > 0.999$ in the vicinity of $m = 0.5$ and $pK_a = -5$. If we use those values we will get a plot with an excellent correlation and a slope of almost exactly 1.0. Does that indicate that the order in $[H_2O]$ is in fact 1 and that there is only one water involved in the transition state of the r.d.s.? Perhaps, but it is more of an indication of the very flat landscape as we alter values of m and pK_a .

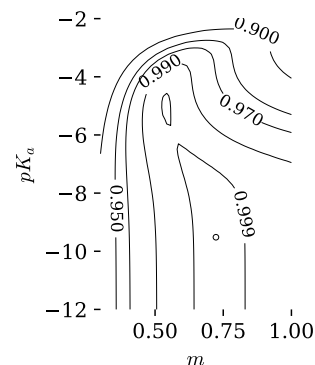


Figure 15: A contour plot of the surface for r^2 as m and pK_a are surveyed. the best fit occurs at $m = 0.72$ and $pK_a = -9.5$ although the surface is very flat for a broad area around those values. ↑

Figure 16: Plot of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ where $m = 0.72$ and $pK_a = -9.5$.

← The line equation is...

$$y = 2.01x + 2.93$$

$$r^2 = 0.999$$

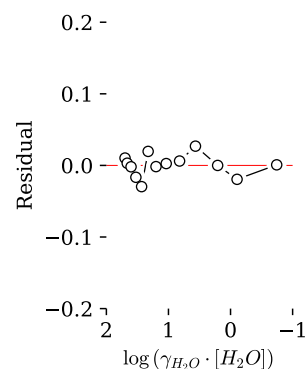
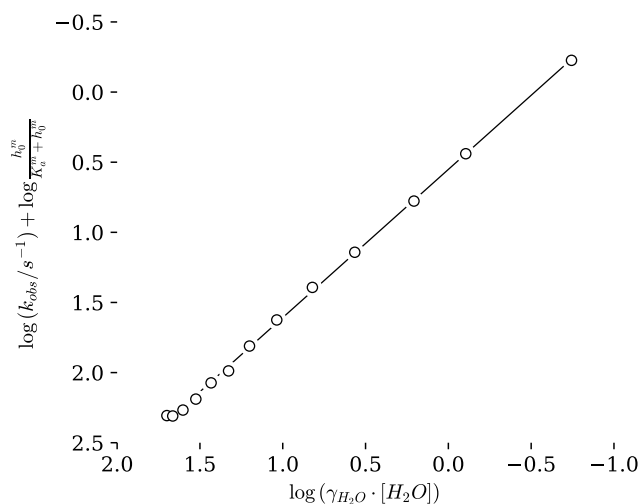


Figure 17: A plot of the residuals. ↑

The *Python* notebook for the plots in Figures 15, 16 and 17 above can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig15-rate_vs_aH2O.ipynb



We need an anchor. The authors proposed that the acidity function for esters in sulphuric acid mixtures would be $0.62H_0$. However they also reported that others had pegged it at $0.65H_0$. There appears to be wiggle-room there. The pK_a value for protonated aliphatic esters are estimated to be in the range of -7 to -8 . The value for pK_a determined from the optimization in figure 15 was well away from those values. Let us compromise on a value for pK_a and set it to -7.5 and then optimize the value of m to achieve the best linear fit.

Optimizing for m with $pK_a = -7.5$

We can vary the value of m while holding $pK_a = -7.5$ and we see that the optimal value for m is 0.676 . This is very close to the reported observations of Lane⁶ and Yates.¹ In figure 21 on the next page we again plot $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ using these parameters and we again get an excellent plot. The plot of the residuals in figure 22 shows a more random distribution. However, if you examine the residual plots so far you may have noticed that the point at the highest concentration of H_2SO_4 (the lowest value for a_{H_2O}) seems to have the largest residual when using pK_a values closer to observations. This point is out at the start of an inflection in the rate curve (see figure 1 of the paper.¹)

Figure 18: Plot of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ where $m = 0.5$ and $pK_a = -5$.

The line equation is...

$$y = 1.06x + 0.55$$

$$r^2 = 0.999$$

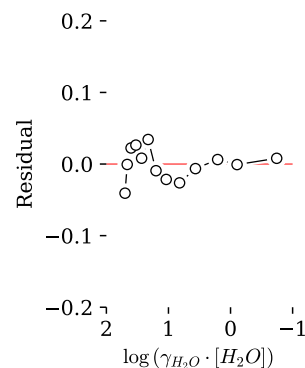


Figure 19: A plot of the residuals. ↑

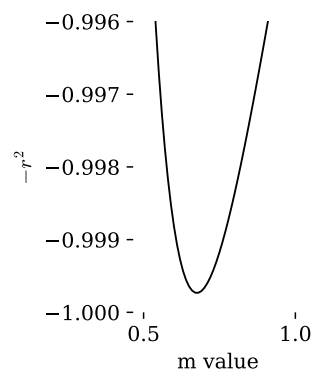


Figure 20: A plot of r^2 as m is varied with $pK_a = -7.5$. The best fit occurs at $m = 0.68$. ↑

The Python notebook for the plots in Figures 18, 19 and 20 above can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig15-rate.vs.aH2O.ipynb and setting the variables of pK_a and m accordingly.

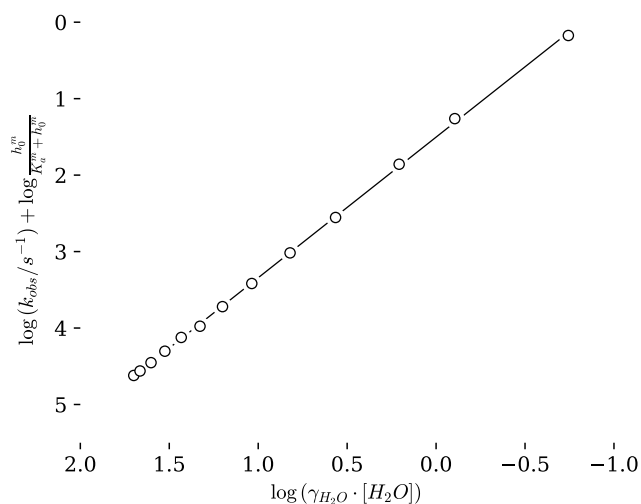


Figure 21: Plot of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ where $m = 0.68$ and $pK_a = -7.5$.

The line equation is...

$$y = 1.84x + 1.50$$

$$r^2 = 0.999$$

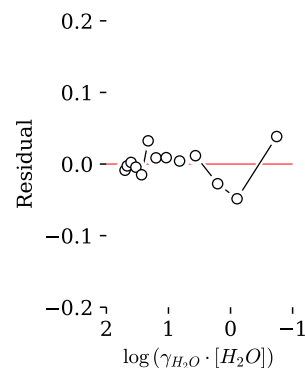


Figure 22: A plot of the residuals. ↑

The *Python* notebook for the plots in Figures 21 and 22 above can accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig20-rate_vs_aH2O.ipynb

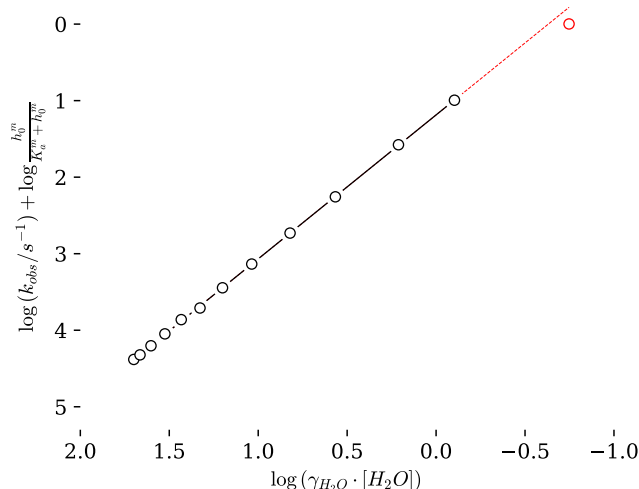
Getting Picky About a Point

Perhaps the point at highest %H₂SO₄ is starting to include a significant amount of the other hydrolysis mechanism that becomes predominant at extreme acid mixtures. The authors do not include it in the line fit for their own determination of the slope when they plotted $\log k_{obs} + mH_0$ vs. $\log a_{H_2O}$ in figure 3 of the paper.

The slight deviation in rate is not great enough to exclude it from the data set using standard statistical tests but, since we see a curve in the plot in figure 3 of the paper, we might use our chemical instinct to justify excluding this last point on the journey to the other mechanism from the data set for the A_{Ac2} mechanism.

We will remove the last data point in table 1 on page 4 and perform an unconstrained optimization of both m and pK_a . The results are displayed in figures 23, 24, and 25 on the following page.

We see in figure 25 that the best fit occurs at $m = 0.69$ and $pK_a = -7.0$. These values are very close to what the authors report from experimental observations. However they must be taken with a grain of salt given the very flat surface of the optimization. The fact that they agree with experiment is very encouraging.



When I plot $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ with $m = 0.69$ and $pK_a = -7.0$ in figure 23, I see another high quality fit with very small and apparently random residuals as shown in figure 24. The order of reaction in $[H_2O]$ is shown to be 2 with the observation of a slope of 1.9 in the plot.

Conclusion

I disagreed with the authors choice of independent variable for their kinetic analysis. The water activity as reported by Giauque et al.² was a mole fraction and not a molar quantity. However the conversion to effective concentration of water made very little difference. It is still the better way to plot the results in my opinion. The authors used experimental observations to establish an acidity function ($0.62H_0$) and a pK_a value of -7.2 for the protonated aliphatic ester. These values gave a slope very near a value of 2 and indicated that the molecularity of water in the r.d.s. is two.

I deleted the single point at highest acidity in the data that was at the beginning of the transition to the other mechanism and, when I optimized the values for the acidity function and the pK_a value without constraints, the values for the acidity function and pK_a for esters was found to be $0.69H_0$ and -7.0 , respectively. The slope was again very near a value of 2.

We have examined and recalculated the results of Yates et al. and, although we used slightly different methods, obtained exactly the same conclusions the authors. Nothing changed — time well spent.

Now use these methods to replot all the data sets in the paper² and confirm that we can get very similar results for the $A_{Ac}2$ mechanism using their data and our own approach.

Figure 23: Plot of $\log k_{obs} - \log \frac{h_0^m}{K_a^m + h_0^m}$ vs. $\gamma_{H_2O} \cdot [H_2O]$ where $m = 0.69$ and $pK_a = -7.0$. The highest $\%H_2SO_4$ point that was excluded is shown in red.

←

The line equation is...

$$y = 1.88x + 1.19$$

$$r^2 = 0.9999$$

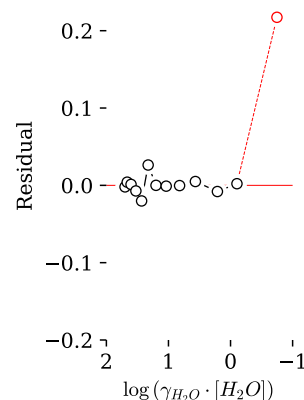


Figure 24: A plot of the residuals. The highest $\%H_2SO_4$ point that was excluded is shown in red. ↑

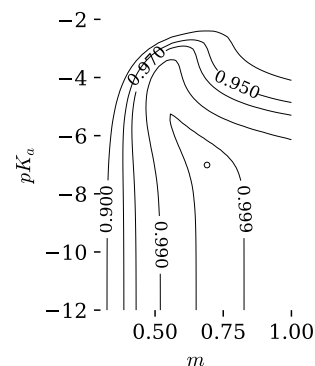


Figure 25: A contour plot of the surface for r^2 as m and pK_a are surveyed when the highest $\%H_2SO_4$ point that was excluded. The best fit occurs at $m = 0.69$ and $pK_a = -7.0$ although the surface is very flat for a broad area around those values. ↑

The *Python* notebook for the plots in Figures 23, 24 and 25 above can be accessed via Google Colab at https://colab.research.google.com/github/blinkletter/4410PythonNotebooks/blob/main/Class_30/Yates-Fig23-rate_vs_aH2O.ipynb