

A Curved Hammett Plot

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Linear free energy relationships are supposed to be linear, and most of the time they are. However, when we have two or more competing pathways or two or more steps in a reaction mechanism, we might observe curved Hammett plots. In this document we will explore an example.

The Hammett Plot

Electrophilic aromatic substitution is a classic mechanism that you will be familiar with. In this experiment, Hart and Sedor investigated the mechanism when the reaction involves intramolecular ring closing.¹ Normally, the addition to the aromatic ring would be rate-determining (k_2 in figure 1.) However, here we have that reaction occurring intramolecularly and that will provide for a much greater rate. Perhaps it will be faster than the formation of the carbocation electrophile and we will see that first step being rate-determining.

The authors synthesized substituted versions of the starting material. The σ values for the substituents are added together to report a total σ value for each polysubstituted reactant. The authors used σ in one region of the Hammett plot and σ^+ in another. They had their reasons, but they did recognize that this made little difference to the quality of the line fits. In this analysis, I will use only σ^+ . The intermediate is a benzyl cation, the very definition of when to use σ^+ . The substituent constants are presented in table 2 and the reactants with their $\sum \sigma^+$ values are described in table 1.

Reactant	X	Y	Z	$\sum \sigma$	$\sum \sigma^+$	k_{obs}
1	H	p-Cl	p-Cl	0.46	0.22	0.096
2	m-CF ₃	H	H	0.43	0.43	0.052
3	m-Cl	H	H	0.37	0.37	0.100
4	H	p-Cl	H	0.23	0.11	0.30
5	m-OCH ₃	H	H	0.12	0.12	0.74
6	H	H	H	0	0	1.00
7	m-CH ₃	H	H	-0.07	-0.07	1.48
8	H	p-CH ₃	H	-0.17	-0.31	3.27
9	H	p-OCH ₃	H	-0.27	-0.78	0.56
10	H	p-CH ₃	p-CH ₃	-0.34	-0.62	5.80
11	H	p-CH ₃	p-OCH ₃	-0.44	-1.09	0.176
12	H	p-OCH ₃	p-OCH ₃	-0.54	-1.56	0.009

¹ "Mechanism of cyclodehydration of 2-phenyltriarylcarbinols", H. Hart, E.A. Sedor, *J. Am. Chem. Soc.*, **1967**, 89, 2342–2347. <https://doi.org/10.1021/ja00986a018>

Figure 1: Cyclization via electrophilic aromatic substitution

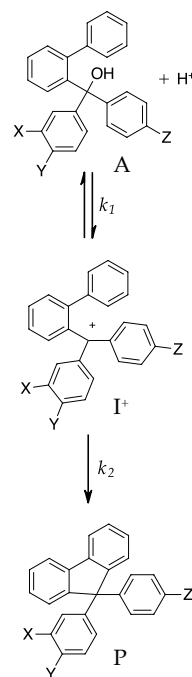


Table 1: Selected substituent constants

A typographical error is present in the data table that was published. The relative value of k_{obs} for reactant 11 was reported to be 1.76 and the value that corresponds to the plotted data in figure 1 of the paper is 0.176.¹ The correct value is used in this analysis.

Table 2: Selected substituent constants.

Substituent	σ	σ^+	σ^-
m-CF ₃	0.43		
p-CF ₃	0.54	0.61	0.65
m-OCH ₃	0.12		
p-OCH ₃	-0.27	-0.78	-0.26
m-CH ₃	-0.07		
p-CH ₃	-0.17	-0.31	
m-Cl	0.37		
p-Cl	0.23	0.11	0.19

The Hammett plot is presented in figure 2. We see a classic example of a change in the rate-determining step. The authors plotted the four points describing a positive slope using σ^+ values and the eight points with a negative slope using σ values. As described above, I chose to use a consistent set of values.²

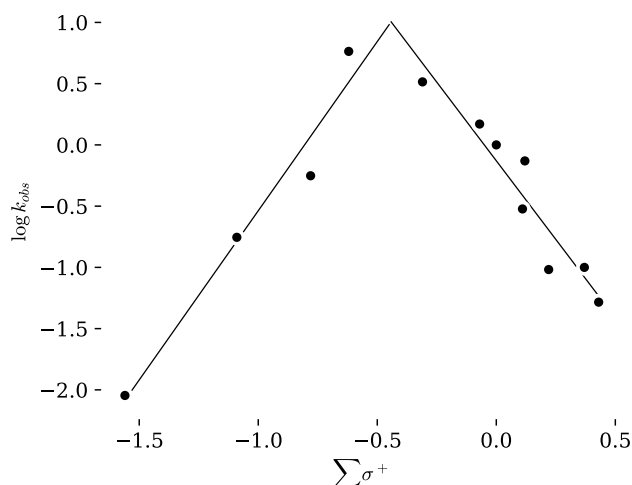


Figure 2: Hammett plot for cyclo-dehydration of substituted 2-phenyl-triarylcarbinols. The author's relative rate data was used with a correction as noted above. The substituent constants were recalculated using the more modern data set of Hansch, Leo & Taft. Only σ^+ values were used. Compare this plot to figure 1 in the paper.¹

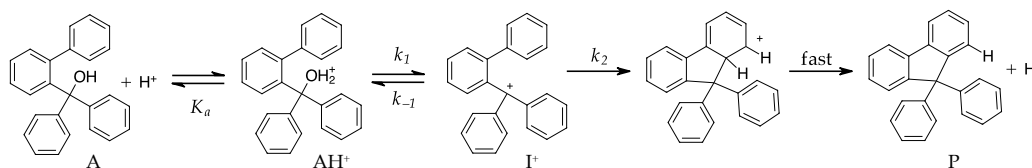
² "A survey of Hammett substituent constants and resonance and field parameters", C. Hansch, A. Leo, R.W. Taft, *Chemical Reviews*, 1991, 91, 165-195. <https://doi.org/10.1021/cr00002a004>. The authors used values from earlier work by Brown & Okamoto.

slightly different

The Mechanism

The mechanism has two steps. First, a tertiary alcohol dissociates in acid to give the carbocation. Second, the cation forms a bond to an aromatic ring via electrophilic substitution. The curved Hammett plot is dominated by the slower step in each region. The step-by-step mechanism is outlined in figure 3

Figure 3: The full proposed mechanism of the reaction.



The first step is an example of specific acid catalysis. Sulphuric acid is a very strong acid and a significant amount of the protonated alcohol will exist at equilibrium. Water is a poor nucleophile, but it is a good leaving group. The triaryl carbocation intermediate is one of the most stable carbocations.

A carbocation is a strong electrophile. In this case, the strong electrophile is held in close proximity to a weak nucleophile (the electron-rich aromatic ring of the biphenyl group.) The intramolecular electrophilic addition to

the aromatic system is rapid. The subsequent deprotonation to recover the aromatic system is rapid. A protonated aromatic ring is one of the strongest acids in organic chemistry.

So we have a carbocation that is easy to make and a subsequent aromatic substitution reaction that is also facile. In your organic chemistry experience, you will have been taught that formation of a carbocation is a rate-determining step and you will also have been taught that addition to a benzene ring is a rate determining step. Which is the r.d.s. here? It appears to change depending on the substituents that affect the electron density of the carbocation intermediate.

The formation of a cation from a neutral starting material will have a negative slope in a Hammett plot. We see that, when the substituents are electron-withdrawing, the formation of the intermediate is the slow step. The slope of the Hammett plot is $\rho = -2.56$. The authors of the paper note that previous work has established that the reaction constant for the equilibrium dissociation of triarylcoldols is $\rho = -3.6$. This is in the same ballpark as the experimental results here. In the transition state, the bond is not fully broken and the ρ value the rate should be less than in the fully dissociate case of the equilibrium.

The electrophilic addition to the biphenyl ring will result in the carbon connected to the substituted rings becoming neutral. The high-energy intermediate is also a carbocation, but the charge is now two atoms further away from the substituted rings. This step has a ρ value of 2.76. This unique situation has resulted in a system where we can change the r.d.s. depending on the substituents in the reactant.

Reaction Kinetics

Reaction kinetics can provide some information to help us interpret these results. Let us take the reaction as the following scheme.



From this scheme we can derive the following rate law.

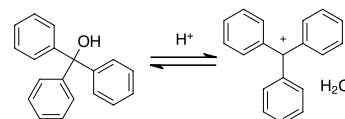
$$v = \frac{[H^+]}{K_a + [H^+]} \frac{k_1}{k_{-1} + k_2} k_2 [A]_t$$

In the case where k_1 is the r.d.s., we say that $k_2 > k_{-1}$. If that is true then the rate law becomes...

$$v = \frac{[H^+]}{K_a + [H^+]} k_1 [A]_t$$

The activity of H^+ has been set in each experiment (4% H_2SO_4) and the only value that will change is the value of k_1 for each substituted

Figure 4: Equilibrium for dissociation of triarylcoldol in strong acid. The reaction constant has been reported to be $\rho = -3.6$ (see reference 10 in the paper.¹)



reactant. The reaction produces a cationic intermediate and we expect a large negative value of the Hammett reaction constant, ρ . So the negative slope region in the curved plot describes the change in the value of k_1 as substituents are changed.

The value of k_1 is increasing as substituents become electron-donating (a more stable cation is easier to make). We also expect k_2 to be diminishing with the same changes (a more stable cation is a weaker electrophile). Eventually k_1 becomes so fast that it is no longer the r.d.s. If we were to state that k_2 is the r.d.s., then we say that $k_2 < k_{-1}$ and the rate law becomes...

$$v = \frac{[H^+]}{K_a + [H^+]} \frac{k_1}{k_{-1}} k_2 [A]_t$$

The k_1/k_{-1} term represents the K_{eq} for formation of the intermediate and the rate of reaction now involves k_2 . As the value of k_2 is reduced by more electron-donating substituents the observed rate will slow also. The positive slope in the curved Hammett plot represents the effect of the change in the value of k_2 as substituents are changed.

Acid Catalysis

Note that the rate law includes a term for the amount of protonated carbinol. The reaction scheme proposes that this is an equilibrium that precedes the r.d.s. That would be specific acid catalysis. Can we confirm this? We generally do not use buffers in strongly acidic systems, so we cannot change the concentration for a buffer to see if the rate increases.

First, we will plot the rate vs acidity for the reactants. When protonation is part of the r.d.s. (either specific or general) we should see a first-order dependance in acid activity. In the reactants that have the aromatic substitution as the r.d.s., we should see no dependance of acid activity.

Second, we will measure the solvent isotope effect on the observed rate. For reactants where the acid is involved in the r.d.s., we should see a kinetic isotope effect. If the acid catalysis is general we should see a significant effect. If the catalysis is specific we will see an inverse solvent kinetic isotope effect (as will be explained below). We will begin with the step one, the acidity rate profile.

Figure 5: Plot of k_{obs} vs H_0 for a series of reactants.

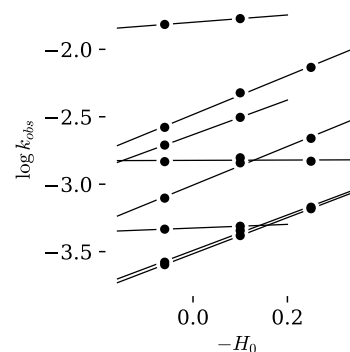


Table 3: Table of literature H_0 values and k_{obs} values for selected reactants.

% H ₂ SO ₄	Literature H_0 values			k_{obs} for selected reactants / $10^{-4}s^{-1}$							
	HOAc ³	Water ⁵	70% DMSO ⁶	1	3	4	5	6	9	10	11
4%	-2.38	0.20	0.06	2.53	2.64	7.88	19.5	26.4	14.7	153	4.64
5%	-2.46	0.09	-0.10	4.16	4.53	14.4	31.3	47.6	15.7	169	4.88
6%	-2.54	-0.02	-0.25	6.58	6.75	21.88		73.5	14.8		

The authors report their observed rates at three concentrations of sulphuric acid, 4, 5 and 6% w/w H_2SO_4 in 80% aqueous acetic acid. To plot rates vs acidity we need a scale that measures acidity, not grams. The authors should have used an indicator dye to determine the H_0 of each mixture. In the absence of that information, I searched the literature looking for reported H_0 values of mixtures of 80% acetic acid and H_2SO_4 . I found none (but I'm not done looking.) I did find a study of H_0 for mixtures of H_2SO_4 and glacial acetic acid.³ I used the data and interpolated H_0 values for each of the three acid conditions. I then used the data reported in table IV of the paper.¹ The data and H_0 values from literature sources are collected in table 3.

The rates were plotted against H_0 values for each reactant. We see in figure 5 that the reactants group into two classes. Those who have nearly identical slopes and those that are independent of acidity. For the reactants where k_{obs} showed a dependence on H_0 , we see a slope in the log-log plot of approximately 2.5. This is greater than second-order. The H_0 values were for mixtures of pure acetic acid and H_2SO_4 . But, the authors performed their experiments in 80% aqueous acetic acid. I could find no H_0 data for that situation.

Hammett has reported that, in aqueous acetic acid, the value of H_0 tracked more closely to the values with water alone.⁴ So I will use H_0 values for $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mixtures. Data is scant for lower concentrations of H_2SO_4 but I found a data set and interpolated H_0 values.⁵ I also found a data set for H_2SO_4 in 70% DMSO,⁶ which seems similar to the water fraction in 80% acetic acid. The log-log plot slopes were 2.0 and 1.3 when these values were used. Without accurate H_0 data for the mixtures used in the paper, we cannot draw any conclusions about the order of the reaction in $[\text{H}^+]$. I feel that the 70% DMSO H_0 values are closest to the answer. This mixture has a similar water fraction in a polar solvent to the case of 80% acetic acid. The absolute acidity will be very different, but the relative acidity across the three concentrations of H_2SO_4 should be similar. This set of H_0 values produced a slope that approached the expected value of 1.0. However, we must be cognizant of confirmation bias and accept that we are doing a bit of "hand waving" here. I expect that if we had directly measured the H_0 of the three concentrations of H_2SO_4 using indicator dyes, we would see an order much closer to 1.

The order of reaction in $[\text{H}^+]$ was calculated from the slopes in figure 5. The slopes were determined against three sets of H_0 values as described above. The results are collected in table 4 and the plots of reaction order (n) vs acidity are presented in figure 6.

We see that the order of reaction has a high magnitude when electron-withdrawing substituents are present and drops to near zero as the system becomes more electron-rich. This tracks with the change in r.d.s. The acid-catalyzed formation of the intermediate (k_1) should have first-order

³ "The Acidity Scale in Glacial Acetic Acid. I. Sulfuric Acid Solutions. —6 < H_0 < 0", N.F. Hall, W.F. Spengeman, *J. Am. Chem. Soc.*, 1940, 62, 2487–2492. <https://doi.org/10.1021/ja01866a062>

⁴ "Acid Catalysis in Sulfuric Acid–Acetic Acid Solutions. The Rate of Bromination of m-Nitroacetophenone", M.A. Paul, L.P. Hammett, *J. Am. Chem. Soc.*, 1936, 58, 2182–2187. <https://doi.org/10.1021/ja01302a027>

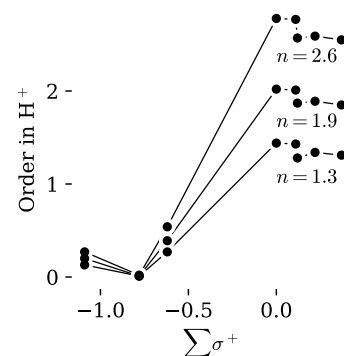
⁵ "Temperature variation of the H_0 acidity function in aqueous sulfuric acid solution", C.D. Johnson, A.R. Katritzky, S.A. Shapiro, *J. Am. Chem. Soc.*, 1969, 91, 6654–6662. <https://doi.org/10.1021/ja01052a021>

⁶ "Acidity Function Behavior in Aqueous–organic Solvents. I. The H_0 and H_A Functions in 70% DMSO/ H_2O ", K. Yates, G. Welch, *Can. J. Chem.*, 1972, 50, 1513–1522. <https://doi.org/10.1139/v72-239>

Table 4: Order of reaction in $[\text{H}^+]$ measured by a plot of $\log k_{obs}$ vs H_0 . Three solvent systems^{3,5,6} that were deemed similar to the experiment are used for the H_0 values.

R	$\sum \sigma^+$	Calculated Order of Reaction		
		HOAc	Water	70% DMSO
1	0.22	2.59	1.89	1.34
3	0.37	2.55	1.85	1.31
4	0.11	2.77	2.01	1.43
5	0.12	2.57	1.87	1.28
6	0	2.78	2.02	1.44
9	−0.78	0.02	0.01	0.01
10	−0.62	0.54	0.39	0.27
11	−1.09	0.27	0.20	0.13

Figure 6: Plot of order of reaction in $[\text{H}^+]$ (n) vs $\sum \sigma^+$ using three different sets of H_0 values.



dependence ($n = 1$) in $[\text{H}^+]$.⁷ The observed values are greater than this. What is clear is that the dependence of rate on $[\text{H}^+]$ drops to zero when the electrophilic aromatic substitution step (k_2) becomes the r.d.s.

Isotope Effects

Solvent isotope effects may provide insight. In general-acid catalyzed reactions, the bond to the proton is breaking or forming (depending on your point of view.) This would have a lower force constant than the covalent bond to the proton on either the acid or the intermediate. We should observe a significant kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} > 1.5$.

If the case is specific-acid catalysis, we have an equilibrium. The bonds to the acid proton are fully formed in both starting material and product. Is there a difference in force constant? Probably, but not enough to matter. However, in water there is another important factor – hydrogen bonding.

The vibrational energy levels of D_2O are lower and the O–D bond is a little stronger than an O–H bond in H_2O . This is also true of the hydrogen bonds in each case; the H-bonds in D_2O are slightly stronger and a bit shorter. D_3O^+ has one H-bonding site now occupied by a proton. This loss of an H-bonding site costs us more in D_2O compared to H_2O .

We conclude that D_3O^+ in D_2O is higher in energy than H_3O^+ in H_2O . That means that it is a stronger acid. $\text{D}_3\text{O}^+/\text{D}_2\text{O}$ with a D_3O^+ concentration of 10^{-7} actually has a $p\text{D}$ value of 6.6⁸ So we would expect about $10^{0.4}$ -fold more protonated intermediate for D_2O compared to H_2O .⁹

The solvent kinetic isotope effects for several of the reactants are reported in table V of the paper¹ and collected in table 5 of this document. We observe that the values reported for $k_{\text{H}}/k_{\text{D}}$ are near $1/2.5$ for cases where the Hammett plot slope is negative (and where k_1 is the r.d.s.) This is exactly what we would expect ($10^{0.4} = 2.5$). So we clearly see an inverse solvent kinetic isotope effect when the r.d.s. is the acid-catalyzed formation of the intermediate. For reactants that have a positive slope (and where k_2 is the r.d.s.) we see that the isotope effect approaches unity.

From the $p\text{H}$ -rate profile and the solvent kinetic isotope effect, we conclude that the formation of the intermediate is rate-determining when the substituents are electron-withdrawing and that this step is specific-acid catalyzed.¹⁰

Thermodynamics

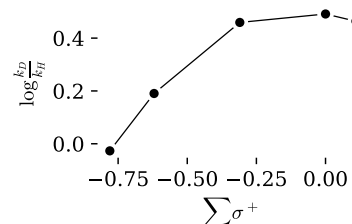
Eyring plots of rate vs temperature experiments will reveal the changes in entropy and enthalpy of the transition state for the r.d.s. The authors report such data in table VII in the paper and the results of the Eyring plots in table I of the paper¹. There is a large change in ΔS^\ddagger as the r.d.s.

⁷ Assuming that $H_0 < K_a$, which is likely true in the aqueous solvent.

Table 5: Solvent Isotope Experiment

Reactant	$k_{\text{D}}/k_{\text{H}}$	$\sum \sigma^+$
4	2.91	0.11
6	3.10	0
8	2.88	-0.31
9	0.94	-0.78
10	1.55	-0.62

Figure 7: Plot of solvent isotope effect vs $\sum \sigma^+$. A significant isotope effect exists when substituents are electron-withdrawing and vanishes as the reactant becomes electron-rich.



⁸ $p\text{H}$ is an acidity function. Although it is defined as $-\log [\text{H}^+]$, it is actually a measure of protonating power. Adding organic solvent will change the $p\text{H}$ even when $[\text{H}^+]$ has not changed. Here we see that same idea with D_2O

⁹ "The Deuterium Isotope Effect", K.B. Wiberg, *Chem. Rev.*, 1955, 55, 713–743. <https://doi.org/10.1021/cr50004a004>

¹⁰ "Application Of The H_0 Acidity Function To Kinetics And Mechanisms Of Acid Catalysis", F.A. Long, M.A. Paul, *Chem. Rev.*, 1957, 57, 935–1010. <https://doi.org/10.1021/cr50017a003>

changes. However, I noted a discrepancy for the most electron-rich reactant (12) in the calculated results for ΔS^\ddagger presented in table I. I will use this data to calculate values for ΔH^\ddagger and ΔS^\ddagger and check to see if there is a typographical error or not. The data is presented in table 6. The Eyring plots are presented in figure 8.

You can see that there are some data series with three or two points. In the paper the authors added back in data points by "extrapolating from Arrhenius plots." I presume that they plotted $\ln k_{obs}$ vs $1/T$ and then used the pre-exponential factor and energy of activation to calculate rates at the temperatures missing data. They then plugged these values into the Eyring plot. Making up data points by extrapolating a two-point plot does not actually get you more data points. You still have two actual points. Obviously, I disagree with this approach and will not be using it. The data in table 6 in this analysis presents only the actual data.

Table 6: Data from table VII of the paper.¹

Temp	<i>spacing</i> k_{obs} for Reactants/ $10^{-4}s^{-1}$											
/ °C	1	2	3	4	5	6	7	8	9	10	11	12
15				1.87	6.39	9.66	12.3	23.3	5.6	53.4		
20	1.26		1.54	3.90	9.88	15.5	21.8	44.5	8.82	99.2	2.79	
25	2.53	1.36	2.64	7.88	19.5	26.4	39.2	86.3	14.7	153	4.64	0.238
30	4.93	2.25	5.06	12.2	33.0	50.4	66.2	137	24.4		8.00	
35	8.89	13.5	9.94	23.8		76.2			36.0			0.701

The Eyring equation relates rate to temperature using transition state theory.

$$k_{obs} = \frac{\kappa k_B}{h} T \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

This can be plotted in the linear form as...

$$\ln \frac{k_{obs}}{T} = \frac{-\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{\kappa k_B}{h} + \frac{\Delta S^\ddagger}{R}$$

Plotting $\ln k_{obs}/T$ vs $1/T$ should result in a straight line with a slope equal to $-\Delta H^\ddagger/R$ and a y-intercept of $\Delta S^\ddagger/R + \ln \kappa k_B/h$.

From the Eyring plot in figure 8, we can see that one data set is clearly out of step with the rest. The data for reactant 2 has an unexpectedly high value for k_{obs} at the highest temperature. Is there a typographical error here? In general, my values for ΔH^\ddagger and ΔS^\ddagger we consistent with the results reported in the paper but there were significant differences. My own interpretation of that data does not show a sudden change in the value for ΔH^\ddagger when the change in r.d.s. is believed to occur but there is a trend in that direction. The values reported by the authors showed a

$$\kappa = 1$$

$$k_B = 1.380649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$$

$$h = 1.054572 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$R = 8.314463 \text{ J} \cdot \text{mole}^{-1} \text{K}^{-1}$$

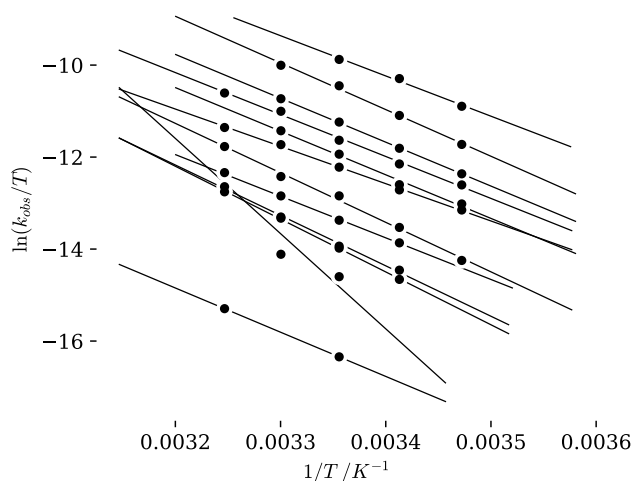


Figure 8: Eyring plot of experimental data from table VII of the paper.¹¹

very clear change. There is no methodology discussed for how curve fits were performed and no documentation of calculations¹¹ provided by the authors.

I also performed the Eyring plot using the data set provided by the authors, including the "extrapolated" points and I did not obtain their values (but was close). The data for reactants 1 and 2 provided very different answers than reported by the authors. I now suspect that there was a typographical error in the extrapolated data for reactant 1 as well as in the experimental data for reactant 2.

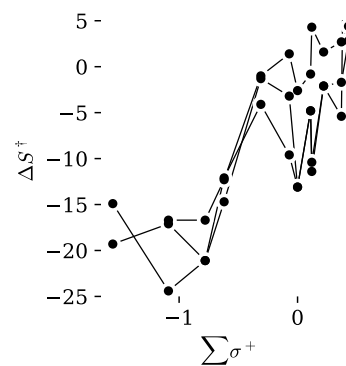
The value for ΔS^\ddagger changes according to the r.d.s. The dissociation step involves separating a group from the molecule, generally splitting a molecule has a positive value for ΔS^\ddagger but in aqueous systems there can be other effects as the departing water is solvated and creates more order in the solvent as hydrogen bonds align. In the case of the values reported by the authors the ΔS^\ddagger for the first step, k_1 , is near zero. In the reactants where the aromatic addition is the r.d.s., we see that ΔS^\ddagger is a significantly negative value. This is expected in ring-closing as we are locking out bond rotations with the ring formation.

My own results using the experimental data only were not as clear cut but still show large negative values where k_2 is the r.d.s. These results and the results calculated from the authors' data with "extrapolated" points are presented in table 7, along with the reported results from table I in the paper.

I plotted these ΔS^\ddagger values against the $\sum \sigma^+$ value for each reactant as shown in figure 9. You can see the trend in ΔS^\ddagger with larger negative values when the r.d.s. is k_2 .

¹¹ See the accompanying *Jupyter* notebook for documentation on my own calculations

Figure 9: Plot of ΔS^\ddagger values against the $\sum \sigma^+$ for the results reported in the paper, results calculated from the edited "extrapolated" data and results calculated from experimental data only.



Reactant	ΔS^\ddagger values			
	$\Sigma \sigma^+$	Extrapolated	From Exp.	Table I
1	0.22	-2.1	-2.1	1.6
2	0.43	2.8	57.8	4.4
3	0.37	-1.7	-5.4	2.7
4	0.11	-4.8	-4.8	-0.8
5	0.12	-10.4	-11.4	4.3
6	0	-13.1	-13.1	-2.6
7	-0.07	-3.2	-9.6	1.4
8	-0.31	-1.3	-4.1	-1.0
9	-0.78	-21.1	-21.1	-16.7
10	-0.62	-14.7	-12.1	-12.3
11	-1.09	-24.4	-17.1	-16.7
12	-1.56	-14.9	-19.3	-4.9

The authors experiment was set over a narrow range of five temperatures. Some reactants only had two data points to make the line. I would recommend at least seven data points for Eyring plots – and make every effort to maximize the accuracy of your observations. Precise temperature control is required along with careful measurements.

Consider if we view the Eyring plots in figure 8 at a scale that includes the y-intercept as shown in figure 10. You can see how far the "dart is thrown" for each curve fit. Small imperfections in the data can change the intercept value significantly. Many researchers consider the Eyring plot unreliable for determining ΔS^\ddagger because of the long-range extrapolation (we are actually extrapolating to infinite temperature and that is a pretty big jump)¹²

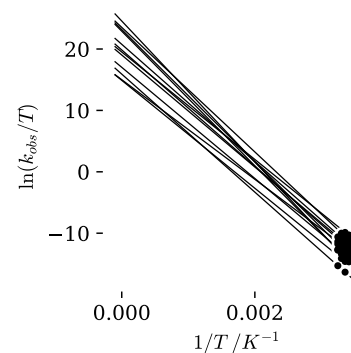
There is another linearization of the Eyring equation that reveals ΔS^\ddagger as the slope, not the intercept. One's instincts say that the slope of five points (a kind of average, really) will be more precise than an extrapolation to the intercept. However, it makes little difference. A mathematical proof of this statistical issue has been published.¹³ In the end, the quality of the data is the most important factor.

Conclusion

The authors have provided evidence that supports their hypothesis that the cyclodehydration of 2-phenyltriarylcarbinol is a reaction that is specific acid catalyzed and that the rate-determining step can change with changing electron density in the aryl rings. The Hammett plot,

Table 7: Data from Eyring plots and Table I of the paper.¹ "Extrapolated" is ΔS^\ddagger values calculated using Eyring plots of the values reported in table VII of the paper. "From Exp" used only the experimental data from table VII. "Table I" is the ΔS^\ddagger values calculated by the authors and reported in table I of the paper. The values in bold were deemed to be likely erroneous and were not included in the plots presented in figure 9.

Figure 10: The Eyring plot from figure 8 scaled to include the y-intercept at $1/T = 0$



¹² How far away do you stand from your dartboard and how reliable is your aim?

¹³ "A common misconception about the Eyring equation", G. Lente, I. Fábíán, A.J. Poč, *New J. Chem.*, 2005, 29, 759-760.
<https://doi.org/10.1039/B501687H>

H⁺ ion molecularity, and solvent kinetic isotope effect all reflect this. Thermodynamic analysis of the kinetics provides the same conclusion, although with less certainty.

Several typographical errors were found or are suspected. The kinetic data does not give the same results as those calculated by the authors (although they are similar) and no documentation as to the computational methods was available to evaluate the reason for this.¹⁴

¹⁴ See the accompanying *Jupyter* notebook for documentation on the data analysis presented in this report. You can spare your readers lots of boring-yet-essential details and provide them with the exact computational methods by using *Jupyter* notebook or similar tools to document your math and methods.