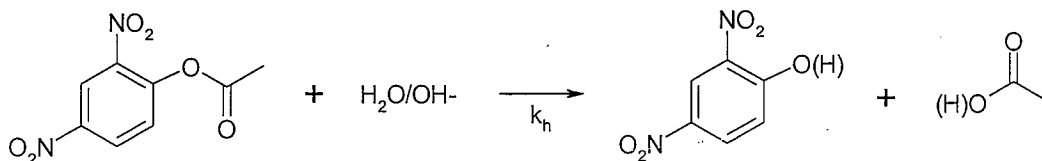


Example Problems in Hydrolysis

Hydrolysis of 2,4-dinitrophenyl acetate (2,4-DNPA): Consider the hydrolysis 2,4-DNPA a compound for which acid catalyzed reaction is unimportant at pH > 2. The following kinetic data was obtained in homogeneous solution at 22.5°C.



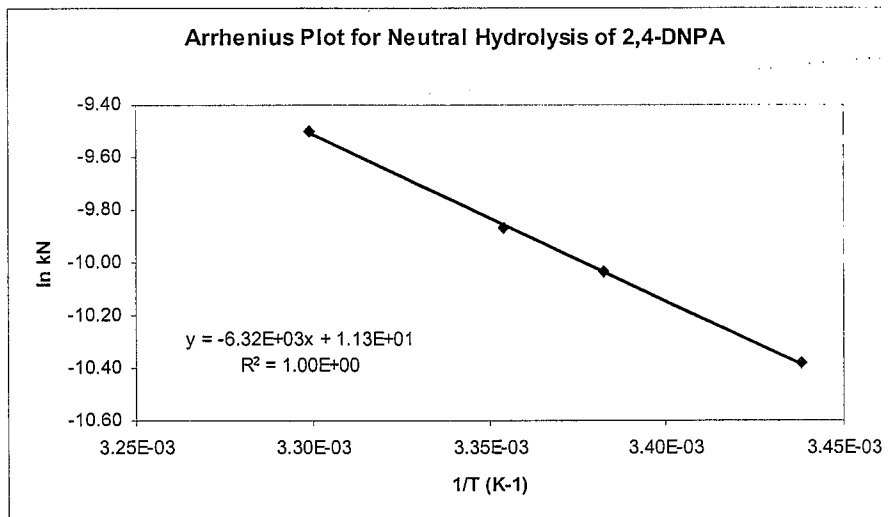
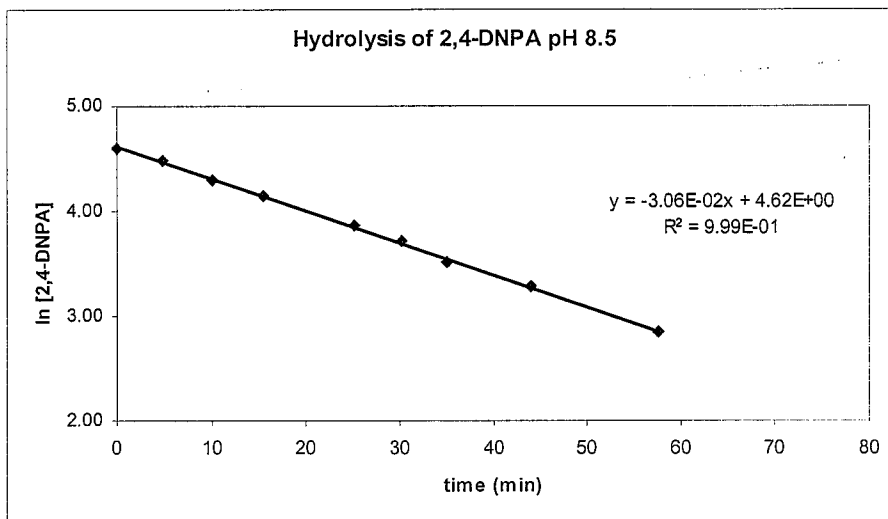
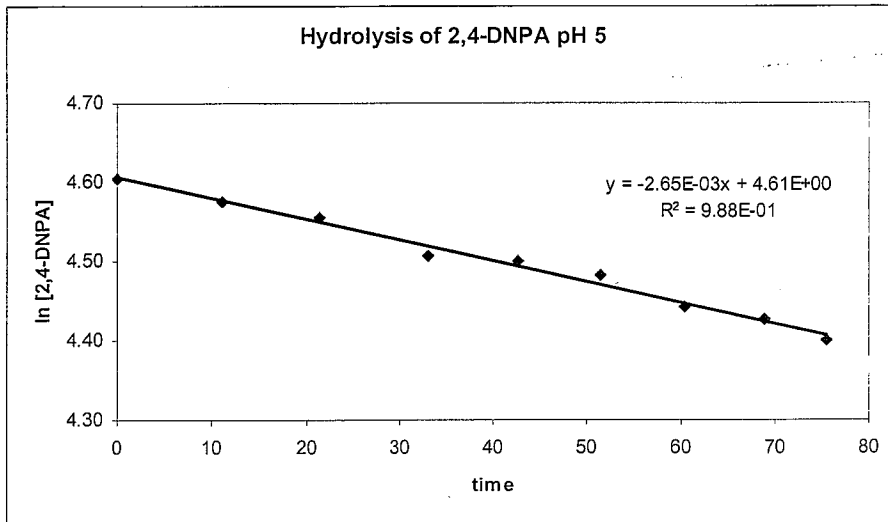
pH = 5.0*		pH = 8.5	
Time (min)	[2,4-DNPA] (μM)	Time (min)	[2,4-DNPA] (μM)
0	100	0	100
11.0	97.1	4.9	88.1
21.5	95.2	10.1	74.3
33.1	90.6	15.4	63.6
42.6	90.1	25.2	47.7
51.4	88.5	30.2	41.2
60.4	85.0	35.1	33.8
68.9	83.6	44.0	26.6
75.5	81.5	57.6	17.3

* similar results were obtained at pH = 4.0 at 22.5°C

- Determine the *pseudo* first order reaction rate constants k_h at pH 5.0 and 8.5.
- Using the data above, derive the rate constants for the neutral (k_N) and base enhanced (k_B) hydrolysis of 2,4-DNPA at 22.5°C.
- At what pH are the two reactions equally important?
- Using the temperature dependent rate constant data, derive the Arrhenius activation energy, E_a for the neutral hydrolysis of 2,4-DNPA.

Temperature (°C)	k_N (s ⁻¹)
17.7	3.1×10^{-5}
22.5	4.4×10^{-5}
25.0	5.2×10^{-5}
30.0	7.5×10^{-5}

- Calculate the time required to decrease the concentration of 2,4-DNPA by hydrolysis to 50% (half-life, $t_{1/2}$) in the epilimnion of a lake ($T = 22.5^\circ\text{C}$, pH = 8.5) and in the hypolimnion of the same lake ($T = 5^\circ\text{C}$, pH 7.5).



$$\text{Rate} = k_h [\text{24-DNPA}]$$

$$\text{where } k_h = k_A[\text{H}^+] + k_N + k_B[\text{OH}^-]$$

but at $\text{pH} > 2$ no acid catalysis

$$\therefore k_h \cong k_N + k_B[\text{OH}^-]$$

Since rate is unchanged between $\text{pH} = 4$ and $\text{pH} = 5$, we can say that $k_N \gg k_B[\text{OH}^-]$ at these pH 's

$$\text{and } \therefore \text{ at } \text{pH} 5, k_h \cong k_N$$

[2,4-DNPA]

So plot $\ln \frac{[2,4\text{-DNPA}]_0}{[2,4\text{-DNPA}]_t}$ vs time at pH to yield a straight line with slope = $-k_h (\cong k_N)$

$$\therefore k_h = 2.65 \times 10^{-3} \text{ min}^{-1} = k_N$$

At $\text{pH} = 8.5$ the reaction is faster and experiences base catalysis. A plot of $\ln [\text{24-DNPA}]$ vs time will yield a straight line with slope = $-k_h (\cong k_N + k_B[\text{OH}^-])$

$$\therefore k_h = 3.06 \times 10^{-2} \text{ min}^{-1}$$

$$\text{so } k_B = \frac{k_h - k_N}{[\text{OH}^-]} = \frac{0.0280 \text{ min}^{-1}}{3.16 \times 10^{-6} \text{ M}} = 8.85 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$$

c) The rates of hydrolysis by the two mechanisms are equal so,

$$k_N [24DNPA] = k_B [OH^-] [24DNPA]$$

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

$$\text{and } [OH^-] = \frac{k_N}{k_B}$$

$$= \frac{2.65 \times 10^{-3} \text{ min}^{-1}}{8.85 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}}$$

$$= 2.99 \times 10^{-7} \text{ M}$$

$$\text{so } pOH = -\log [OH^-]$$
$$= 6.52$$

$$\text{and } pH = pK_w - pOH$$

$$= 14.00 - 6.52$$

$$= 7.48$$

d) The Arrhenius equation relates rate constants to temperature

$$k = A e^{-E_a/RT}$$

where A is a pre-exponential factor
 E_a is the activation energy
 R is universal gas constant
 T is absolute temperature

$$\text{So } \ln k = \ln A - \frac{E_a}{RT}$$

and a plot of $\ln k$ vs $\frac{1}{T}$ will yield a straight line with slope = $-\frac{E_a}{R}$

$$\text{Slope} = -6320 \text{ K}$$

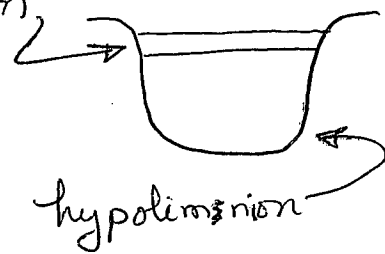
$$\therefore E_a = -(-6320 \text{ K})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$= 52,500 \text{ J mol}^{-1} \quad (52.5 \text{ kJ/mol})$$

e) $t_{1/2}$ = half life

$$= \frac{\ln 2}{k_h}$$

epilimnion



At pH 8.5 and $T = 22.5^\circ\text{C}$

we know $k_h = 3.06 \times 10^{-2} \text{ min}^{-1}$

$$\text{so } t_{1/2} = \frac{0.693}{3.06 \times 10^{-2} \text{ min}^{-1}} = 22.6 \text{ mins}$$



At pH = 7.5 and $T = 5^\circ\text{C}$

we need to calculate the value of k_N and k_B at 5°C using Arrhenius Eqn.
For this, we will assume the same activation energy (E_a).

$$\text{Since } \ln k_h = -\frac{E_a}{RT} + \ln A$$

we can derive

$$\ln\left(\frac{k_{h,T_2}}{k_{h,T_1}}\right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For k_N ;

$$\ln\left(\frac{k_{N,T_2}}{k_{N,T_1}}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $T_1 = 278.2$

$$T_2 = 295.7$$

$$k_{N,T_1} = 2.65 \times 10^{-3} \text{ min}^{-1}$$

$$k_{N,T_2} = ?$$

solving for $k_{N,T_2} = 6.60 \times 10^{-4} \text{ min}^{-1}$

Similarly for k_B at 5°C

$$k_{B,T_2} = 2.32 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$$

Recall, $k_h = k_N + k_B[\text{OH}^-]$

$$\text{so } k_h = 6.60 \times 10^{-4} \text{ min}^{-1} + 2.32 \times 10^3 \text{ M}^{-1} \text{ min}^{-1} [\text{OH}^-]$$

at 5°C , $\text{p}K_w = 14.73$

and $\text{p}[\text{OH}^-] = \text{p}K_w - \text{pH} = 7.23$

$$\therefore [\text{OH}^-] = 10^{-7.23} = 5.89 \times 10^{-8} \text{ M}$$

So,

$$k_h = 6.60 \times 10^{-4} \text{ min}^{-1} + 2.32 \times 10^3 \text{ M}^{-1} \text{ min}^{-1} (5.89 \times 10^{-8} \text{ M})$$
$$= 7.80 \times 10^{-4} \text{ min}^{-1}$$

and $t_{1/2} = \frac{0.693}{7.80 \times 10^{-4} \text{ min}^{-1}} = 880 \text{ mins}$

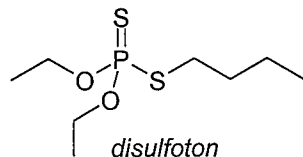
or 14.8 hrs

Note :

at pH 7.5 and 5°C the hydrolysis is dominated by the neutral rxn mech. and is ≈ 40 times slower

than the hydrolysis at pH 8.5 and 22°C

Hydrolysis of an Insecticide in a River: In 1986, 3500 kg of the insecticide *disulfoton* were introduced in the Rhine river ($T = 11^{\circ}\text{C}$, $\text{pH } 7.5$) during an accident in Switzerland. You want to determine how much of the *disulfoton* will be eliminated by abiotic hydrolysis over the 8 days 'travel time' to the Dutch border.

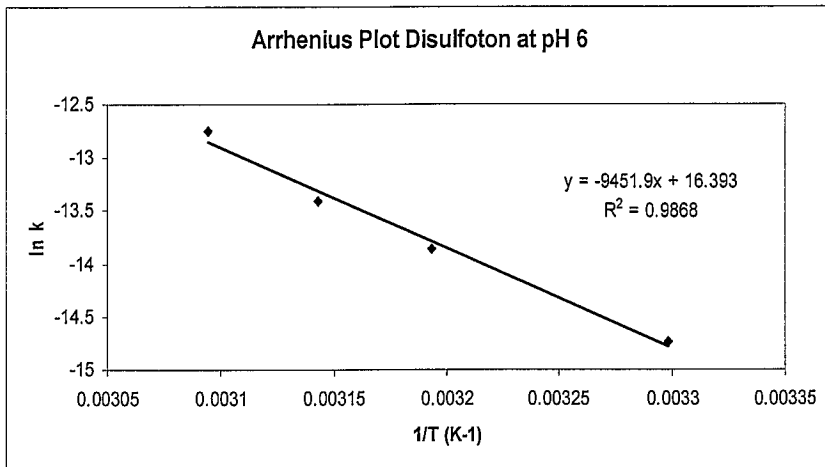


Since you do not find any good kinetic data in the literature, you decide to make your own measurements in the laboratory. Under all selected experimental conditions, you observe *pseudo* first order kinetics and obtain the following results.

Temperature ($^{\circ}\text{C}$)	k_{obs} (s^{-1})		
	pH 6.0	pH 11.98	pH 11.72
20		1.3×10^{-5}	
30	$4.0 \times 10^{-7*}$		3.6×10^{-5}
40	9.6×10^{-7}		
45	1.5×10^{-6}		
50	2.9×10^{-6}		

* a similar k_{obs} was obtained at $\text{pH } 4.0$ at 30°C

- How much *disulfoton* will have been lost by abiotic hydrolysis in 8 days?
- What is (are) the most likely hydrolysis product(s)?



Ionization Constants for Water

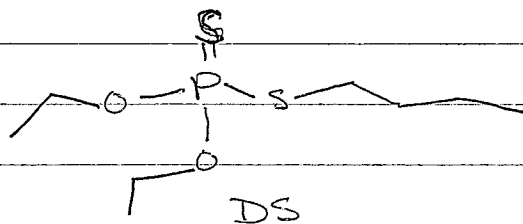
Temperature (°C)	pK _w
0	14.9435
5	14.7338
10	14.5346
15	14.3463
20	14.1669
24	14.0000
25	13.9965
30	13.8330
35	13.6801
40	13.5348
45	13.3960
50	13.2617
55	13.1369
60	13.0171

(CRC Handbook)

Q2

Disulfoton

Hydrolysis rate at pH 7.5
 $T = 11^\circ\text{C}$



$$\text{Rate} = k_h [\text{DS}] \quad 1^{\text{st}} \text{ order (pseudo)}$$

$$\text{In general, } k_h = k_A[\text{H}^+] + k_N + k_B[\text{OH}^-]$$

$$\text{but rate (pH=4)} = \text{rate (pH=6)}$$

\therefore assume no acid catalysis in this range

$$\text{and } k_h \approx k_N \text{ at pH 6}$$

$$k_N = 4.0 \times 10^{-7} \text{ s}^{-1} \text{ at pH=6, } T = 30^\circ\text{C}$$

~~we~~ use Arrhenius Eqn. to determine k_N at pH=6
 $T = 11^\circ\text{C}$

plot $\ln k_N$ vs $1/T$

$$\text{slope} = -9452 \text{ K} = \frac{-E_a}{R}$$

$$E_a = -(-9452 \text{ K})(8.314 \text{ J/mol K})$$

$$E_a = +78,580 \text{ J/mol} = 78.6 \text{ kJ/mol}$$

$$E_a = 78,580 \text{ J mol}^{-1}$$

$$\ln \left\{ \frac{k_2}{k_1} \right\} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$k_2 \Rightarrow \text{at } 11^\circ\text{C} = 284.2 \text{ K} \leftarrow T_2$$

$$k_1 = 4.0 \times 10^{-7} \text{ at } 30^\circ\text{C} = 303.2 \text{ K} \leftarrow T_1$$

$$\ln \left\{ \frac{k_2}{4.0 \times 10^{-7}} \right\} = -\frac{78,580 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{284.2} - \frac{1}{303.2} \right)$$

$$= -2.084$$

$$\therefore \ln k_2 = -2.084 + \ln 4.0 \times 10^{-7}$$

$$= -16.82$$

$$\therefore k_2 = e^{-16.82} = 4.97 \times 10^{-8} \text{ s}^{-1}$$

↖
RN at 11°C , $\text{pH}=6$

find k_B using data at $pH = 11.72$

$$k_h = k_N + k_B [OH^-]$$

at $30^\circ C$, $pH = 11.72$; $k_h = 3.6 \times 10^{-5} s^{-1}$

& at $30^\circ C$, $k_N = 4.0 \times 10^{-7} s^{-1}$

so $k_B = \frac{k_h - k_N}{[OH^-]}$

~~at~~ $[OH^-] = 10^{\cancel{14.0 - pH} - pOH}$

$$pOH = pK_w - pH$$

$$= 14.0 - 11.72$$

$$= 2.28$$

$$[OH^-] = 10^{-2.28} = 5.25 \times 10^{-3} M$$

$$\text{So } k_B = \frac{3.6 \times 10^{-5} s^{-1} - 4.0 \times 10^{-7} s^{-1}}{5.25 \times 10^{-3} M}$$

$$= 6.78 \times 10^{-3} M^{-1} s^{-1} \text{ at } 30^\circ C$$

Assume same E_a as for k_N

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

\swarrow $78,580 \text{ J mol}^{-1}$
 \nwarrow ?
 \uparrow $6.78 \times 10^{-3} M^{-1} s^{-1}$ \uparrow 284.2 K \uparrow 303.2 K

$$\ln k_2 = -2.084 + \ln 6.78 \times 10^{-3} = -7.077$$

$$\therefore k_2 = e^{-7.077} = 8.43 \times 10^{-4} M^{-1} s^{-1}$$

At $T = 11^\circ\text{C}$

$$k_N = 4.97 \times 10^{-8} \text{ s}^{-1}$$

$$k_B = 8.43 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_h = k_N + k_B [\text{OH}^-]$$

and at $\text{pH} = 7.5$, $[\text{OH}^-] = 10^{-(\text{p}K_w - \text{pH})}$
 $= 10^{-(14.5 - 7.5)} = 10^{-7.0}$
 $= 1.0 \times 10^{-7} \text{ M}$

$$\therefore k_h = 4.97 \times 10^{-8} \text{ s}^{-1} + 8.43 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} (1.0 \times 10^{-7} \text{ M})$$

$$= 4.98 \times 10^{-8} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{4.98 \times 10^{-8} \text{ s}^{-1}} = 1.39 \times 10^7 \text{ s} = \frac{16.1 \text{ days}}{\cancel{38.16 \text{ hr}}}$$

$$\ln \left\{ \frac{[\text{DS}]}{[\text{DS}]_0} \right\} = -k t \leftarrow 8 \times 24 \times 60 \times 60 = 6.91 \times 10^5 \text{ s}$$

$$\therefore \ln \frac{[\text{DS}]}{[\text{DS}]_0} = \frac{4.98 \times 10^{-8} \text{ s}^{-1}}{\uparrow} \times 6.91 \times 10^5 \text{ s} = -0.0344$$

$$\frac{[\text{DS}]}{[\text{DS}]_0} = e^{-0.0344} = 0.966$$

$$[\text{DS}] = 0.966 [\text{DS}]_0$$

$\therefore \approx 3400 \text{ kg}$
remains
after 8 days.