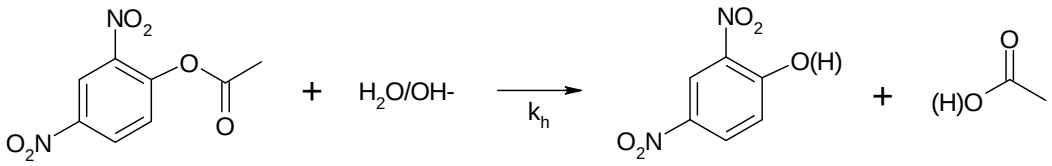
Example Problems in Hydrolysis

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

a) Determine the *pseudo* first order reaction rate constants k_h at pH 5.0 and 8.5.

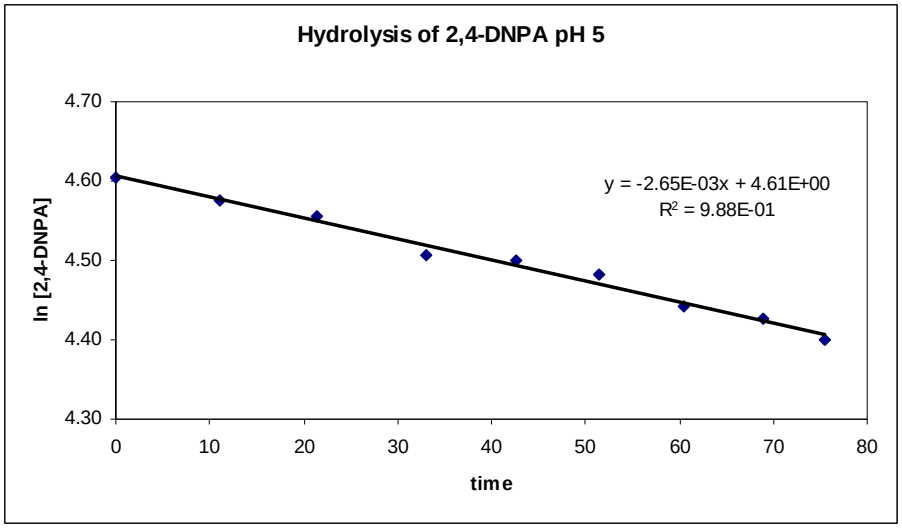
b) Using the data above, derive the rate constants for the neutral (k_N) and base enhanced (k_B) hydrolysis of 2,4-DNPA at 22.5°C.

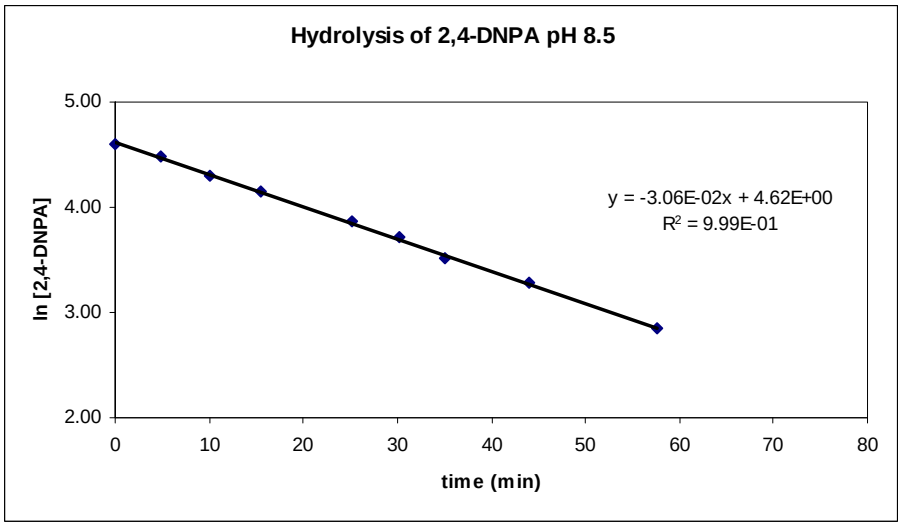
c) At what pH are the two reactions equally important?

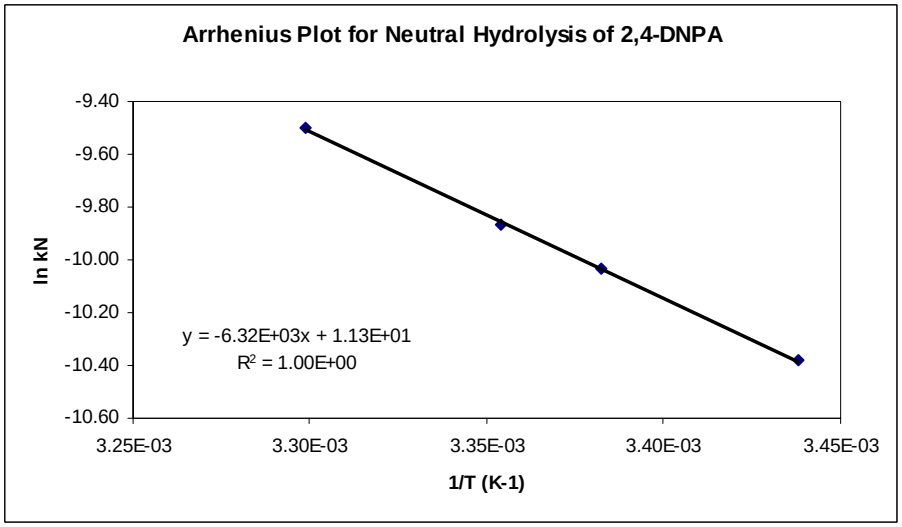
d) Using the temperature dependent rate constant data, derive the Arrhenius activation energy, E_a for the neutral hydrolysis of 2,4-DNPA.

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}

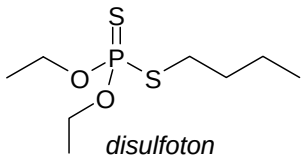
e) Calculate the time required to decrease the concentration of 2,4-DNPA by hydrolysis to 50% (half-life, $t_{1/2}$) in the epilimnion of a lake (T = 22.5°C, pH = 8.5) and in the hypolimnion of the same lake (T = 5°C, pH 7.5).


Hydrolysis of 2,4-DNPA pH 5
ln [2,4-DNPA]
4.70
4.60
4.50
4.40
4.30
0
10
20
30
40
50
60
70
80
time
y = -2.65E-03x + 4.61E+00
R² = 9.88E-01


Hydrolysis of 2,4-DNPA pH 8.5
ln [2,4-DNPA]
5.00
4.00
3.00
2.00
0
10
20
30
40
50
60
70
80
time (min)
y = -3.06E-02x + 4.62E+00
R² = 9.99E-01


Arrhenius Plot for Neutral Hydrolysis of 2,4-DNPA
ln kN
-9.40
-9.60
-9.80
-10.00
-10.20
-10.40
-10.60
3.25E-03
3.30E-03
3.35E-03
3.40E-03
3.45E-03
1/T (K-1)
y = -6.32E+03x + 1.13E+01
R² = 1.00E+00

Hydrolysis of an Insecticide in a River: In 1986, 3500 kg of the insecticide *disulfoton* were introduced in the Rhine river (T = 11°C, 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.



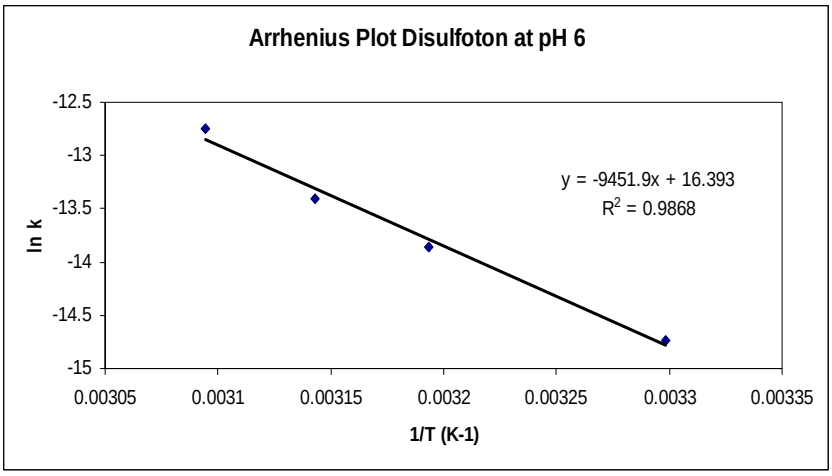
disulfoton

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 (°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 pH 4.0 at 30°C

a) How much *disulfoton* will have been lost by abiotic hydrolysis in 8 days?
b) 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)