Kinetics of Chemical Reactions

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Abstract

In my project I researched rate law for different reaction orders to draw some conclusions about the nature of the reactions. I then completed an experiment with the hydrolysis of carbaryl and applied the data to my mathematical equations.

Introduction

Kinetics is a part of chemistry that deals with rates, orders, half-lives, and mechanisms. Reaction rate, a'(t), is the "speed" of a reaction, expressed as concentration over time. Mechanisms explain the chemical steps of a reaction. Half lives, $t_{1/2}$, are the amount of time required for half the original amount of substance to remain. Reaction order explains the relationship between concentrations and rate, expressed as an exponent n. Rate constants are a positive coefficient in a rate expression specific to a reaction, expressed as k. Concentration, a(t), is expressed in moles per liter or molarity. General rate expression dependent on one reactant:

Methods

I worked with Dr. Dedeian to complete the experimental portion of this project. I used a spectrophotometer to measure absorbance of my solution over time. On the spectrophotometer I ran my experiment with the kinetics mode, which measures absorbance at a set wavelength against time. I then converted the absorbance values to concentration values to use in my equations. I expected to see a decreasing concentration as time progressed.

I created a stock solution from the solid carbaryl by adding this to methanol to dissolve it. I add 0.5 mL of this solution to a pH buffer. For my experiment I tested two buffers; one at pH 10.55 (top graph) and another at pH 10.98 (bottom graph). After mixing the stock solution and buffer I fill a cuvette and place it into the spectrophotometer to measure the absorbance at 279





500.0000



 $a'(t) = -k[a(t)]^n$

use this general expression and set n to orders 0,1,2, and 3 to integrate the expression. After integration, I solve the differential equations for each of the following reaction constants.



nanometers for 20 minutes.

Results

The data for each reaction when put into the rate constant equations are shown. For both reactions, the second order equation had the most consistent set of solutions, so the rate order is second order.

When averaging out the rate constant values, the rate constants for pH 10.55 and pH 10.98

> respectively are: $k_{avg} = 5.54 \cdot 10^{-4}$ $k_{avg} = 10.3 \cdot 10^{-4}$

I can further prove the reaction is second order using half-life. Time for one half life should be proportional to the inverse of the original amount and the rate constant. pH 10.98 reached its first half-life: (0.00s, 1.4079M) -> (674.10s, 0.7040M)

hu 10.22						
TIME (s)	CONC. (M)	n = 0	n = 1	n = 2		
0	1.2655	-	-	-		
21	1.2479	0.838095	6.669125	53.07029		
42	1.2314	0.811905	6.503707	52.10073		
50.4	1.2246	0.811508	6.518461	52.36443		
100.1	1.1865	0.789211	6.439511	52.56094		
150.5	1.149	0.774086	6.416964	53.23622		
200.2	1.1122	0.765734	6.449913	54.40428		
250.6	1.0768	0.752993	6.44348	55.25781		
300.3	1.0494	0.719614	6.235389	54.18714		
350	1.0227	0.693714	6.086317	53.60067		
400.4	0.9946	0.676573	6.016032	53.7532		
450.1	0.9687	0.659409	5.937961	53.79023		
500.5	0.9438	0.642757	5.860306	53.81519		

pH 10.98 TIME (s) CONC. (M) n = 0 n = 1

accurate results with my experimental data. I confirmed the order with the half-life expression for second order: $t_{1/2} = \frac{1}{k_2 \cdot a_o}$ Where k_2 is the rate constant from the trial using pH of 10.98 and a_o is the initial concentration of the solution. I also concluded that reaction order holds higher importance than reaction rate as the two

reactions had the same order, since they used the same mechanism, but different rates. The second

Conclusion

Both reactions produced results of second order.

This shows how the derived equations created

My experiment was a **base-catalyzed hydrolysis** reaction with the chemical carbaryl. Carbaryl is a chemical found in pesticides. It contains the carbamate functional group, which targets insects' nervous systems. In hydrolysis reactions, water displaces a functional group, in this case the carbamate group. It is a unimolecular reaction; meaning the rate is dependent on one concentration value, being the carbaryl concentration in the reaction.



Now that I know the order and constant, I can write the rate expression with concentration as a variable for pH 10.55 and pH 10.98

respectively: $a'(t) = -5.54 \cdot 10^{-4} [a(t)]^2$ $a'(t) = -10.3 \cdot 10^{-4} [a(t)]^2$

Where the second expression has a faster

decreasing rate.

0	1.4079	-	-	-
21	1.3664	1.97619	14.24747	102.7257
42	1.3328	1.788095	13.05172	95.29143
50.4	1.3203	1.738095	12.74608	93.50377
100.1	1.2495	1.582418	11.92365	89.95246
150.5	1.179	1.52093	11.78954	91.62704
200.2	1.1096	1.49001	11.89309	95.3786
250.6	1.0496	1.429769	11.71948	96.75426
300.3	0.9997	1.359307	11.40191	96.57755
350	0.9532	1.299143	11.14371	96.80573
400.4	0.9075	1.24975	10.96806	97.81485
450.1	0.8625	1.211731	10.8869	99.78729

1.17962

0.8175

500.5

n = 2

102.4903

10.86121

trial with pH 10.98 used a more basic buffer, and since the reaction is **base-catalyzed** it proceeded at a faster decreasing rate.

To continue this project, I would use a constant pH value and change the initial amount of substance to see how this would affect the rate. I would also run the experiment longer to get a second half life, $t_{3/4}$, to further confirm if the reaction is second order

Acknowledgements and References

Dr Trubnik, Dr. Dedeian, Bristol Myers Squibb

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