

Fundamentals of Hydrolysis: Kinetics of Carbaryl Hydrolysis

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Introduction: During 2000, 293 billion pounds of about 8000 different organic compounds were manufactured in the United States (1). Many millions of pounds of synthetic organic compounds are deliberately introduced into the environment for weed and pest control, and many millions of pounds of other chemicals are introduced into the environment through their proper uses. However, an increase in production and dispersion of synthetic organic chemicals is reported to be responsible for species extinction and several hundred thousand of human cancers per year (2). Several years ago, the government began to regulate the manufacture and use of selected chemicals, such as DDT, which had been shown to be exceptionally hazardous to the biological environment (3). In addition, federal registrations such as the Toxic Substance Control Act regulate the introduction of hazardous chemicals into the environment (3).

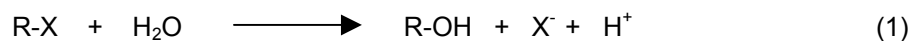
Fortunately, the environment has the capacity to transform many kinds of chemicals through a variety of chemical and biological degradative processes (4). In aquatic systems, reaction of a compound with water ("hydrolysis") is perhaps the most important and significant chemical degradative process since many hydrolysable chemicals, including pesticides and plasticizers, eventually find their way into groundwater, streams, and rivers through leaching and runoff (4). In addition, hydrolysis by-products are normally less toxic to organisms than parent compounds. The rates of hydrolysis in aquatic systems are greatly dependent on environmental factors such as sunlight, microbial populations, and oxygen supply (5). Researchers in environmental chemistry investigate the effects of some of the key environmental factors such as pH, temperature, solvent composition, metal ion catalysis (mineral components), ionic strength and buffer effects (5). In this case study, one such experiment explores the effect of pH on the hydrolysis reaction of a commonly used insecticide.

Question 1: Discuss why hydrolysis reactions are important and significant processes in the aquatic environment.

Question 2: What are important parameters that affect the rates of hydrolysis in the environment?

Hydrolysis Background:

Hydrolysis is a transformation process in which an organic molecule, RX, reacts with water, forming a carbon-oxygen bond (oxygen atom of water molecule) and cleaving a carbon-X bond in the original molecule. The products of a hydrolysis reaction are usually less of an environmental concern than the parent compounds because the products are usually more polar compounds that are less hydrophobic than the original molecules and therefore behave differently in the environment (6). The net reaction is commonly defined as a direct displacement of X by OH:



Where X can represent a variety of functional groups. Pesticides that are derivatives of carboxylic acids have functional groups that are subject to hydrolysis. For this

case study we are studying a derivative known as a [carbamate](#) which involves an amide and ester linkage.

Chemists have identified many mechanisms that can be classified as hydrolysis reactions. March (1985) lists eight mechanisms for ester hydrolysis. We will consider only three of those mechanisms that chemists have classified based on pH. In the case of acid-catalyzed hydrolysis, an acid, usually a proton (H^+) catalyzes the bond breaking and bond making process. Because the proton is not consumed in the reaction, the process is referred to as acid-catalyzed hydrolysis. The rate of the reaction depends on the proton concentration; thus, the rate increases as the pH decreases. Acid-catalyzed hydrolysis is dominant below pH 6. In the case of base-mediated hydrolysis, hydroxyl (OH^-) behaved as a [nucleophile](#) and is consumed in the reaction. This pathway is often referred to as alkaline hydrolysis. The rate of reaction depends on the hydroxyl concentration and increases with increasing pH. Alkaline hydrolysis is dominant above pH 7 or 8. In the third type of hydrolysis, the rate of reaction is independent of the acid-base concentration (pH independent). This process is often referred to as neutral hydrolysis. Neutral and alkaline hydrolysis are the most common reactions within the pH range common to the environment (8).

The process of hydrolysis can be distinguished from several other possible reactions between organic chemicals and water such as elimination, addition to carbon-carbon bonds, isomerization, and decarboxylation. In such types of reactions, oxygen atom or water molecule is not incorporated into the transformation product; consequently, these reactions are not hydrolysis reactions even if they do occur in water (9).

Question 3: Explain the differences between hydrolysis and other chemical reactions.

Hydrolysis mechanism for carbaryl:

Acid-catalyzed hydrolysis is not an important mechanism for carbaryl because as a carbamate the central carbon atom is surrounded by two electron-withdrawing atoms (oxygen and nitrogen). See [Figure 3](#). The protonation of the carboxyl oxygen would not greatly improve the appeal of the central carbon atom to a nucleophile. Very little research has been conducted on the neutral hydrolysis mechanism for carbamates, although it could be important at pH values found in the environment.

Alkaline hydrolysis is an important mechanism for carbaryl and other carbamates. For carbaryl, which has hydrogen as the R_1 substituent (see [Figure 3](#)), an elimination step is the slow step and determines the rate of hydrolysis. For other carbamates that have an alkyl group as the R_1 substituent, formation of a tetrahedral intermediate is the [rate-determining step](#). The alkyl group at R_1 also makes the rate much slower than if hydrogen were present.

Hydrolysis kinetics:

The rate law for hydrolysis is usually defined by a simple [pseudo-first order reaction](#).

$$-\frac{d(RX)}{dt} = k_h [RX] \quad (2)$$

$$-\frac{d(RX)}{dt} = k_b [OH^-][RX] + k_a [H^+][RX] + k_N [H_2O][RX] \quad (3)$$

where $[RX]$ is the molar concentration of the chemical,
 k_h is the observed pseudo-first order rate constant for hydrolysis at a given
 pH,
 k_B is the alkaline second order rate constant,
 k_A is the acid-catalyzed second order rate constant, and
 k_N' is the neutral second order constant.

By taking into account the acid-catalyzed, neutral, and alkaline hydrolysis reaction,
 we can express the observed pseudo-first order reaction as:

$$k_h = k_B[OH^-] + k_A [H^+] + k_N'[H_2O] \quad (4)$$

and since $[H_2O]$ generally remains constant, we can simplify equation 4 to;

$$k_h = k_B[OH^-] + k_A [H^+] + k_N \quad (5)$$

In this equation, k_A , and k_B are the second-order reaction rate constants for acid-catalyzed, alkaline-hydrolysis, respectively, and k_N is the first order rate constant for neutral hydrolysis (the alkaline and acid-catalyzed rate constants have the dimensions of $M^{-1}s^{-1}$ and the neutral rate constant has the dimensions of s^{-1}) (11).

At equilibrium,
$$K_w = [H^+] [OH^-] \quad (6)$$

thus,
$$[OH^-] = K_w/[H^+] \quad (7)$$

Substituting equation 7 into equation 5 yields,

$$k_h = \frac{k_B K_w}{[H^+]} + k_A [H^+] + k_N \quad (8)$$

Equation 8 shows how the pH affects the overall rate of hydrolysis. At high or low pH (high OH^- or H^+) one of the first two terms is usually dominant, while at pH 7 the last term may be the most important. However, the detailed relationship of pH and rate constant depends on the specific values of k_A , k_B , and k_N . Each separate rate constant indicates a stoichiometric relationship between the compounds to be hydrolyzed and the reactants (acid, base, or water), but it does not indicate the detailed mechanism or pathway, which may change from one class to another (11).

As can be seen from equation 8, the hydrolysis reaction is strongly dependent on the pH. A slight change in pH causes a large change in the rate of reaction and/or the hydrolysis [half-life](#). When a reaction follows first-order kinetics, the concentration decreases exponentially with time. According to equation 2, a plot of the natural log of concentration ($\ln[RX]_t$) versus time will vary linearly with a slope of $-k_h$. This slope and the rate are dependent on the concentration. The hydrolysis [half-life](#), the time required for 50% of the compound to disappear, will be determined for first-order and pseudo-first order reactions by (12):

$$t_{1/2} = \frac{\ln(2)}{k_h} \quad (9)$$

The larger the overall rate of reaction, the smaller the half-life will be obtained.

Question 4: To appreciate the effect of pH on the hydrolysis rate constant or half-life, plot the half-life of the following compounds as pH changes. Use the information given in Table 1 along with equations 8 and 9.

Table 1: Hydrolysis rate constants for two carboxylic acid esters

Name	Structure	Acid-catalyzed rate constant, k_A ($M^{-1}s^{-1}$)	Neutral rate constant, k_N (s^{-1})	Alkaline rate constant, k_B ($M^{-1}s^{-1}$)
Ethyl acetate	$CH_3-\overset{\overset{O}{\parallel}}{C}-OCH_2CH_3$	1.1×10^{-4}	1.5×10^{-10}	1.1×10^{-1}
Methyl dichloroacetate	$CHCl_2-\overset{\overset{O}{\parallel}}{C}-OCH_3$	2.3×10^{-4}	1.5×10^{-5}	2.8×10^3

Research Objective:

As part of a masters research project in environmental chemistry, kinetic data on the hydrolysis of [carbaryl](#), an [insecticidal carbamate](#), were collected ([13](#)). The objective was to determine the hydrolysis rate constant at pH values between 6 and 10.

Read through the information about the experimental methods and examine the results. Answer some questions about the collected data. Test yourself on what you have learned about hydrolysis, kinetics, and carbaryl.

Experimental Approach and Methods:

The rates of hydrolysis of carbaryl were measured in deionized-distilled water at 4 pH values (6, 7, 9, 10). Each piece of glassware used in the experiment was sterilized by an autoclave. During the experiment, 500-mL of solution were adjusted to the desirable pH values by addition of buffer solutions. Appropriate amounts of carbaryl stock solution were then transferred to individual tubes, and the pH of the solution was measured again. The pH of the solution was measured before and after each round of sampling to ensure that the pH remained constant during the experiment. The vials were capped with Teflon-faced septum and incubated in a water bath at 25°C, which was kept in the dark to minimize photolysis. Ten mL aliquots were taken from each vial at time zero (approximately 1 hour after incubation) and subsequent time intervals, then transferred to 12 mL vial. Subsequently, the pH was immediately dropped to approximately 3 by adding phosphoric acid to minimize the hydrolysis reaction. Three-mL aliquots of the adjusted sample were removed and transferred into a 4 mL HPLC autosampler vial. The further addition of 1.0-mL of an internal standard ([carbofuran](#)) was spiked into each vial. The samples were analyzed [by high performance liquid chromatography \(HPLC\)](#) with detection by [UV-visible spectrometry](#). The spectrometer was set to monitor effluent at a wavelength of 280 nm. HPLC is used rather than [gas chromatography](#) because carbaryl is sensitive to high temperatures.

Results:

The overall half-lives from the experimental data are summarized in [Table 2](#).

Question 5: Use the data from [Table 2](#) to calculate the overall rate constants (k_h) of carbaryl at the given pH. Use s^{-1} as the units for the rate constants.

Question 6: Use equation 8 and the k_h values obtained from Question 5 to calculate the specific rate constants for neutral and alkaline hydrolysis. (Hint: Remember that acid-catalyzed hydrolysis is not important for carbaryl.)

Question 7: From [Table 2](#), explain why there are differences between the observed half-lives obtained in this experiment and those cited from the literature.

Test Your Knowledge Quiz

1. There is only one mechanism known for the hydrolysis of organic compounds.
True or False
2. Usually hydrolysis reactions are important for environmental contaminants because the products of hydrolysis are
 - a) more toxic
 - b) more non-polar
 - c) less easily transported
 - d) less toxic
3. The important hydrolysis mechanisms for carbamates that have hydrogen rather than a carbon-centered group at the R_1 location include:
 - a) alkaline hydrolysis
 - b) acid-catalyzed hydrolysis
 - c) neutral and alkaline hydrolysis
 - d) all of the above
4. pH is an important factor in determining the kinetics of the hydrolysis of carbamates because
 - a) the rate increases with temperature
 - b) OH^- acts as a nucleophile
 - c) H^+ acts as an inhibitor
 - d) H_2O acts as an electrophile
5. For carbamates, the hydrolysis rate constant increases as the
 - a) pH increases
 - b) pH decreases
 - c) temperature decreases
 - d) ionic strength increases
6. The overall hydrolysis rate constant for carbaryl is
 - a) first order
 - b) second order
 - c) pseudo-first order
 - d) pseudo-second order
7. Carbaryl is likely to be persistent in acidic waters.
True or False

8. The solutions were kept in the dark during the experiment to prevent
- photolysis
 - reduction
 - oxidation
 - isomerization
9. The alkaline hydrolysis rate constant was smaller than the neutral hydrolysis rate constant for carbaryl.
True or False
10. The major products of hydrolysis for carbaryl are
- carbon dioxide and ethanol
 - carbon dioxide, naphthol, and ethanol
 - carbon dioxide, methylamine and ethanol
 - carbon dioxide, naphthol, and methylamine

Answers to quiz (for instructors' use only)

- False
 - d
 - c
 - b
 - a
 - c
 - True
 - a
 - False
 - d
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Answers for the questions

Question 1: Discuss why hydrolysis reactions are important and significant processes in the aquatic environment.

Hydrolysis is an important and significant reaction in the environment because:

- The hydrolysis by-products are more polar and less toxic than parent compounds.
- Because they are more polar, the hydrolysable compounds are less persistence in the soil surface and be leaching into groundwater, streams, or runoff into the waterway.
- The rates of hydrolysis in the aqueous systems are independent on uses of chemicals but rapidly changeable in indicators of the degaradative capacity of aquatic systems, such as sunlight, microbial population, and oxygen supply.

Question2: What are important parameters that affect the rates of hydrolysis in the environment?

The environmental factors that affect the rates of hydrolysis are:

- pH
- temperature
- solvent composition
- mineral components

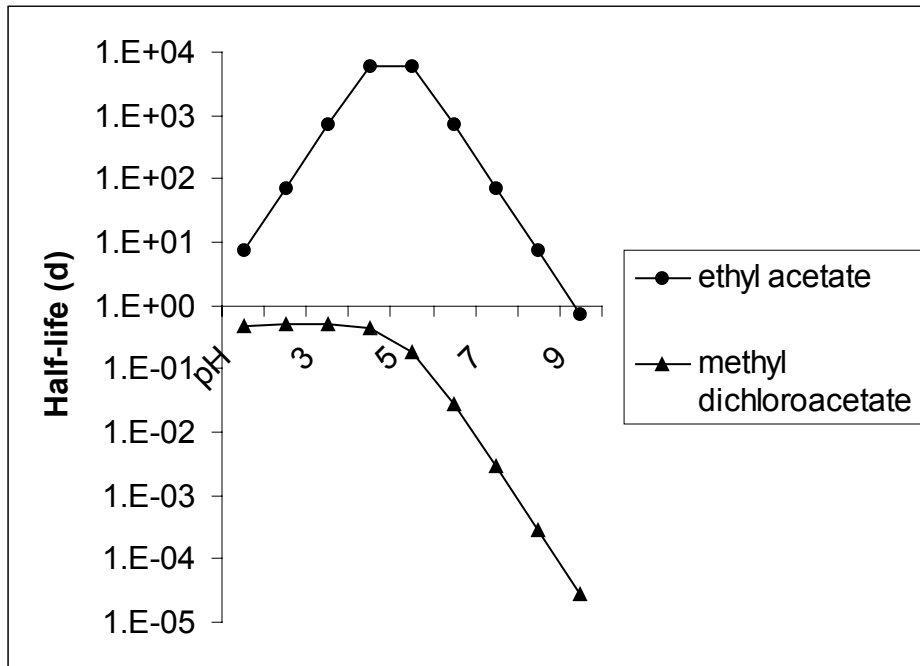
- e). concentration of chemicals
- f). ionic strength and buffer effect.

Question 3: Explain the differences between hydrolysis and other chemical reactions.

The hydrolysis reaction is the bond making and bond forming process with the association of an oxygen atom (from water molecule) incorporated into hydrolysis transformation product.

Question 4: To appreciate the effect of pH on the hydrolysis rate constant or half-life, plot the half-life of the following compounds as pH changes. Use the information given in Table 1 along with equations 8 and 9.

Use equation 8 and the information provided in the Table 1 to calculate the pseudo-first order rate constant for the two carboxylic acid esters from pH 2 to pH 10. Use the results to calculate the half-lives using equation 9. Plot the half-life versus pH for each ester. The figure below should result.



Question 5: Use the data from Table 2 to calculate the overall rate constants (k_h) of carbaryl at the given pH. Use s^{-1} as the units for the rate constants.

pH	Half-life (observed)	Overall rate constant (k_h)
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	(day)	(s ⁻¹)
6	192.500	4.17 x 10⁻⁸
7	44.9421	1.79 x 10⁻⁷
9	0.193	4.16 x 10⁻⁵
10	0.026	3.09 x 10⁻⁴

Question 6: Use equation 8 and the k_h values obtained from Question 5 to calculate the specific rate constants for neutral and alkaline hydrolysis. (Hint: Remember that acid-catalyzed hydrolysis is not important for carbaryl.)

Assume that there is no contribution from the acid-catalyzed rate constant (k_A) for carbaryl. Also, assume that the neutral rate constant (k_N) is so small that at pH 10 only the alkaline rate constant (k_B) contributes to the overall hydrolysis rate constant (k_h). Therefore, at pH 10

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

Using $k_h = 3.09 \times 10^{-4} \text{ s}^{-1}$ and $[\text{OH}^-] = 1 \times 10^{-4}$, k_B is equal to $3.09 \text{ M}^{-1}\text{s}^{-1}$. Also assume that only k_N is responsible for the k_h at pH 7. Therefore, $k_N = 1.79 \times 10^{-7} \text{ s}^{-1}$. You can check these assumptions by checking the results at pH 9.

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

Using the k_B and k_N determined above and $[\text{OH}^-] = 1 \times 10^{-5}$ results in $k_h = 3.11 \times 10^{-5} \text{ s}^{-1}$. This answer is relatively close to the measured kinetic rate constant at pH 9 of $4.16 \times 10^{-5} \text{ s}^{-1}$. You can also check the assumption that the acid-catalyzed rate constant is unimportant by solving for k_A at pH 6.

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

Using $k_h = 4.17 \times 10^{-8} \text{ s}^{-1}$, $k_N = 1.79 \times 10^{-7} \text{ s}^{-1}$, $k_B = 3.09 \text{ M}^{-1}\text{s}^{-1}$, $[\text{H}^+] = 1 \times 10^{-6}$, and $[\text{OH}^-] = 1 \times 10^{-8}$, the equation results in a negative number for k_A . This is an indication of the insignificance of acid-catalyzed hydrolysis for carbaryl.

Question 7: From [Table 2](#), explain why there are differences between the observed half-lives obtained in this experiment and those cited from the literature.

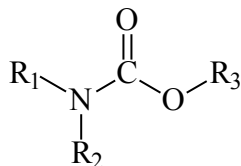
The differences between the observed half-lives and the half-lives from the literature may be due to:

- Differences in temperature,
- Experimental errors,
- Different experimental procedures,
- Analytical errors, and
- Random errors.

Standard deviations for the rate constants should be examined to determine if the differences are real.

Glossary

Carbamates are a group of pesticides derived from carbamic acid (HO-CO-NH₂).



The R₁ and R₂ are hydrogens or carbon-centered groups and R₃ is a carbon-centered group. The carbamates were introduced in the early 1950s by the Swiss company, Geigy Chemical Company. They have the same mode of action as [organophosphate](#) pesticides, which is inhibition of an enzyme, **cholinesterase**, vital to the nervous system. [Carbaryl](#) and [carbofuran](#) are carbamate pesticides.

Carbaryl or 1-naphthyl methylcarbamate is a [carbamate](#) insecticide, which was initially available in the mid-1950s. It is the most widely used carbamate. It is sold under the tradename of Sevin and is used in the lawn and garden area to control insects. It has an oral LD₅₀ of 307 and a dermal LD₅₀ of 2,000 (Ware, 1978). For more information see:

<http://www.speclab.com/compound/c63252.htm>

<http://pmep.cce.cornell.edu/profiles/extoxnet/carbaryl-dicrotophos/carbaryl-ext.html>

Carbocation is a hydrocarbon, which contains a central carbon atom with 3 other groups attached and bearing only 6 electrons. This results in a positively charged species.

Carbofuran or 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate is a [carbamate](#) insecticide. It is also used as a nematicide, which is used to kill microscopic roundworms that attack the roots of crops. Carbofuran is not licensed for home use. It has an oral LD₅₀ of 8 and a dermal LD₅₀ of 10,200 (Ware, 1978).

Electrophiles are electrons deficient species that seek out electron rich areas and are capable of accepting a pair of electrons to form a new covalent bond.

Gas chromatography (GC) is a separation technique that uses gas as a mobile phase and a liquid or solid as a stationary phase coated on a column. Organic compounds are separated because of their different interactions with the stationary phase. Different devices are available for the detection of the compounds as they exit the column. **ECD** is an electron capture detector. **FID** is a flame ionization detector.

Half-life is the time required for 50 percent of the compound to disappear.

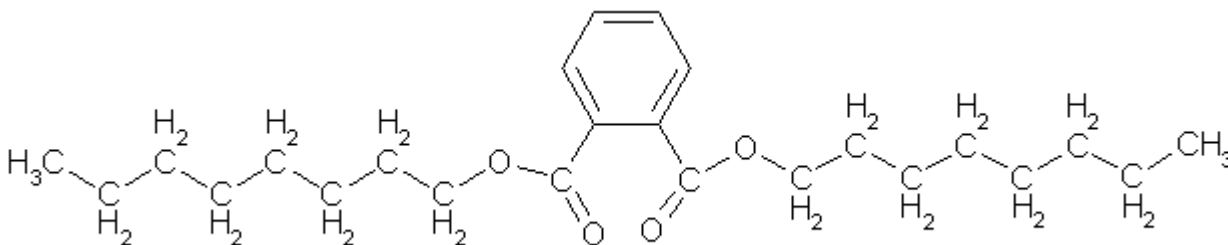
HPLC (high-performance liquid chromatography) is an analytical technique for mixtures that uses liquid as a mobile phase and use liquid or solid as a stationary phase. Analytes are separated based on their affinity for the column that serves as the stationary phase. The essential components include a pump or pumps, sampling valves and loops, a separation column, a detector, and a readout device. Various detectors can be used in conjunction with the HPLC including **UV-vis spectrometer**, fluorescence detectors, and electrochemical detectors.

Organochlorine pesticides are some of the first organic pesticides that were developed after World War II. The organochlorine pesticides do not belong to a single class of chemical compounds but range from chlorinated aliphatic hydrocarbons to cyclodienes. Many of the organochlorine pesticides have been banned in the U.S. such as DDT, endrin, dieldrin, and chlordane. However, DDT is still used in many tropical areas because of its effectiveness against malaria bearing insects.

Organophosphate pesticides are pesticides derived from phosphoric acid esters. They are mainly used as insecticides although a few are used as herbicides and fungicides. Common organophosphate pesticides include malathion, methyl parathion, parathion, phorate, terbufos, and disulfoton. Organophosphate pesticides are subject to hydrolysis which decreases their persistence in the environment. They are generally more toxic to vertebrates than [organochlorine insecticides](#).

Pesticide is a substance or material used to control, prevent, destroy, repel, or mitigate any undesirable or unwanted fungi, plants, insects, or any organisms. This generic term is used to describe fungicides, algicides, herbicides, insecticides, rodenticides, and other substances

Plasticizer is a chemical agent that is added to a polymer to make it softer and more flexible. These are usually small molecules with dangling bits that can disrupt the packing of polymer chains. A common plasticizer used to soften polyvinyl chloride (PVC) is dioctyl phthalate.



Pseudo first order is a reaction in which the concentrations of all but one of the reactants are so large that they change little over the course of the reaction; or in other words, these concentrations are constant at a given system.

For example, the rate of cometabolic biotransformation of some halogenated organic compounds or biological transformation can be expressed as:

$$-dC/dt = kCX$$

where C is the concentration of organic compound transformed
 X is the concentration of bacteria
 Minus sign (-) represents the disappearance of organic

compounds

During biotransformation process, X might be so large that it does not change during the reaction; subsequently, X can be considered as a constant and the rate of expression becomes:

$$-dC/dt = k'C$$

where k' is equal to kX . The reaction in this form is typically termed a pseudo-first-order reaction with k' being the pseudo-first-order rate constant.

Nucleophiles are electron rich species that seek out electron deficient areas and are capable of donating a pair of electrons to form a new covalent bond.

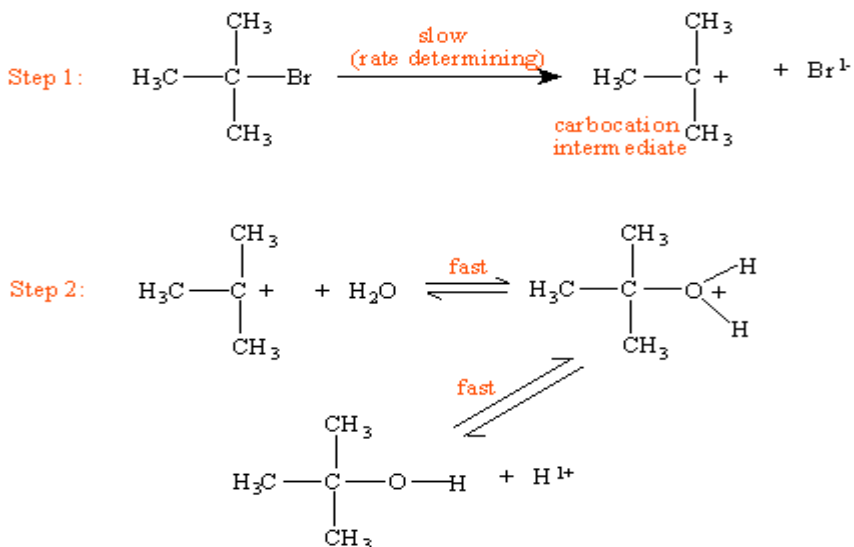
Rate-determining step: The rate-determining step is the slowest step in a multi-step reaction. It determines the overall rate constant for the reaction because it has the transition state with the highest free energy.

S_N1 (unimolecular nucleophilic substitution) is a mechanism that occurs in at least two distinct steps. The first step is that the leaving group leaves with the formation of a carbocation. The second step is that the nucleophile donates electrons to neutralize the carbocation and make a new bond to carbon. The S_N1 mechanism depends on the formation of a carbocation.

The general trends of S_N1 mechanism are:

- A). Leaving groups located in a primary position NEVER undergo S_N1 reactions
- B). Leaving groups located in a secondary position can undergo S_N1 reactions, but it depends on the structure and other factors.
- C). Leaving groups located in a tertiary position ALWAYS undergo S_N1 reactions, compared to S_N2 reactions

The mechanism of S_N1 reaction



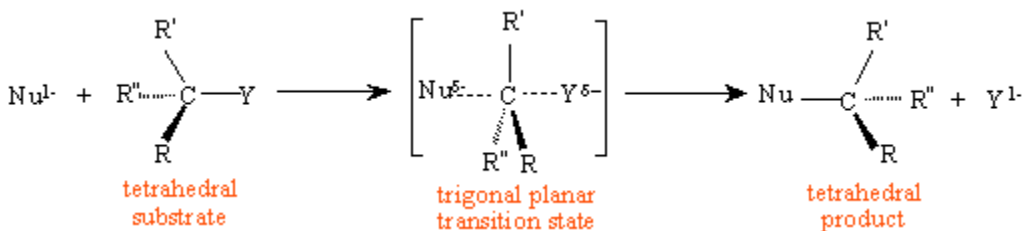
The major factors affecting the rates of S_N1 reactions are substrate, nucleophile, leaving group, and solvent system

S_N2 (bimolecular nucleophilic substitution) is a mechanism where a substitution takes place all in one step. The leaving group departs and the nucleophile attaches at the same time. The S_N2 reaction occurs when the nucleophile can easily approach the carbon; however, it fails to occur when there is a lot of crowding around that carbon. The S_N2 reaction is very sensitive to steric hindrance.

The general trends of S_N2 mechanism are

- A). Leaving groups located in a primary position easily undergo S_N2 reactions.
- B). Leaving groups located in a secondary position can undergo S_N2 reactions, but it depends on the structure and other factors.
- C). Leaving groups located in a tertiary position do NOT undergo S_N2 reactions.

The mechanism of S_N2 mechanism:



The major factors affecting the rates of S_N2 reactions include substrate, nucleophile, leaving group and solvent system.

An ultraviolet/visible spectrophotometer is an analytical instrument that is designed to measure the amount of light absorbed at wavelengths characteristic of ultraviolet and visible region. Further information about UV/visible spectroscopy can be found at <http://www.onu.edu/A+S/chemistry/ultra.html> and <http://www.imp.mtu.edu/matchar/uv.html>.

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Table 2: Summary of the Overall Rate Constants for Each pH.

pH	Half-life (observed) (day)	Half-life(day) (Faust and Gomma, 14)
6	192.500	N/A
7	44.942	10.5
9	0.193	0.104
10	0.026	0.0104