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Determination of Activation Energy for the Thermal Degradation of Poly(vinyl chloride) and Its Practical Applications

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Abstract

In the following experiment, the activation energy of thermal dehydrochlorination of polyvinyl chloride will be determined and the applications of the activation energy will be explored. PVC samples were exposed to various temperatures. For each temperature the rate of reaction was determined through the production of HCl. The rate constant of the reaction was graphically determined using the graph of ln[HCl] vs t, where the slope of the graph was rate constant, k. Using those rate constant values, the activation energy was graphically determined using a graph of ln(k) vs. t^{-1} obtained from the linearized Arrhenius equation. After the activation energy was determined, the implications of the data were analyzed. PVC is susceptible, like all plastics, to thermal degradation. The rate at which PVC degrades at lower temperatures was determined using an alternative form of the Arrhenius equation. A new rate constant value was used to estimate the lifespan of PVC under said conditions. Various methods to increase thermal resistance of PVC were reviewed, including the addition of stabilizers to PVC and the use of CPVC in more demanding environments.

Background

Polyvinyl Chloride (PVC) is a widely produced synthetic plastic. There are numerous applications of the plastic, as it is a versatile, long lasting material [1]. From construction, to healthcare, PVC accounts for approximately 20% of all manufactured plastics [4]. Like all plastics, PVC is limited by its tendency to become softer at high temperatures (thermally degrade). If thermal degradation goes unidentified, severe mechanical/structural failures are likely to occur [5]. Certain measures, such as adding stabilizers to the material, can be taken to increase the “stability” or ability to resist thermal degradation of a plastic [2]. However, it is essential to further understand the mechanisms in which PVC thermally degrades. Identifying the functional lifespan of PVC would allow manufacturers and clientele to estimate the serviceability of the material across various industries.

This functional lifespan can be predicted by one such quantity; the activation energy. In a specific chemical reaction, the activation energy describes the minimum amount of energy a reacting species must possess to undergo a reaction. Activation energy can be simply thought of as an energy barrier, in which a reaction must overcome this barrier to proceed [8]. The importance of this value can be made clear by the Arrhenius equation [9]: $k = Ae^{\frac{-E_a}{RT}}$

Where,

k = Reaction Rate Constant

A = Frequency Factor

e = Euler’s Number (Numerical Constant)

E_a = Activation Energy

R = Universal Gas Constant

T = Temperature (Kelvins)

Activation energy and rate of reaction are closely related as shown by the correlation between k and E_a. Knowing the activation energy allows one to further understand the reaction being observed. Estimating the serviceability of a PVC sample involves the understanding of the chemical reaction PVC undergoes during its degradation, and obtaining experimental values indicating the rate of reaction of PVC [9]. Let’s investigate the former.

PVC is produced through the polymerization of vinyl chloride monomers as shown below [11]:

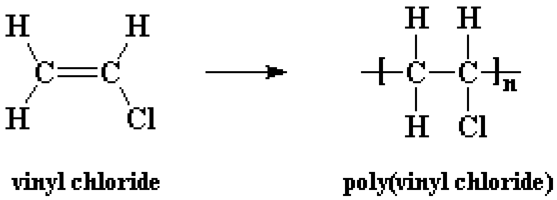


Figure 1

During its lifespan, the plastic experiences degradation and its structural integrity is compromised. The degradation of PVC is known as a dehydrochlorination reaction, where chlorine splits from the polymer in the form of hydrogen chloride. The following chemical equation describes the reaction [11]:

$n[-CH_2-CHCl-CH_2-HCl-] \underset{\blacktriangle}{\rightarrow} HCl + n[-CH_2CHCl-CH=CH-]$

According to this equation, the amount of HCl produced directly relates to the rate of thermal degradation of PVC. Rate of thermal degradation can then be determined through experimental means, and with the Arrhenius equation, can graphically provide the activation energy. An alternative form of the Arrhenius equation can be used to relate the varying rate constants [9]:

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

Where,

k_2 = Reaction Rate Constant at Low Temperature (T_1)

k_1 = Reaction Rate Constant at High Temperature (T_2)

E_a = Activation Energy

R = Universal Gas Constant

T_2 = Low Temperature Value

T_1 = High Temperature Value

Once the rate constant at a certain temperature is experimentally determined, the activation energy of the reaction can be used to calculate the rate constant at varying temperatures. The alternative Arrhenius equation displays this relation quantitatively, but one can understand this relation intuitively. Activation energy universally describes the energy required to initiate a reaction and thus, does not change with temperature, with this knowledge, one can use the activation energy as a tool of relation to determine an unknown rate constant at a temperature that was not experimentally viable.

In this experiment, the rate of degradation of PVC at high temperatures is an experimentally measurable rate of reaction. At lower temperatures, the degradation of PVC is prolonged to such an extent that it is impossible to measure in a timely manner. It is far more reasonable to determine the rate constant at a high temperature and use the original Arrhenius equation to determine the activation energy of the reaction. This activation energy can then be used to determine the lower temperature rate constant. The rate constant at lower temperatures can be used to estimate the lifespan of PVC in it's environment.

The following experiment will involve the determination of activation energy of the thermal dehydrochlorination of polyvinyl chloride through experimental means. The rate constant will be determined at various temperatures. The rate constant will be used in the Arrhenius equation to determine the activation energy graphically. Once the activation energy is determined, it will be used to find the rate constant at a lower temperature (which serves to emulate service conditions) and the lifespan of the PVC sample at exposure temperatures will be estimated.

Determining Activation Energy

Generally, determining the activation energy of a reaction requires the conduction of experiments which measure the rate of reaction at various temperatures. Using the Arrhenius equation, a plot of ln(k) vs. 1/T will have a slope of Ea/R (R being the gas constant 8.314 J/mol-K).

Materials

-Erlenmeyer/Conical Flask
-Beaker
-Argon Gas
-PVC Samples
-Oil Bath

-Heat Source
-Test Tubes
-Rubber Stoppers (with airlock hole)
-Water Bath

-Titrator
-NaOH

Experimental Apparatus

Prepare an oil bath to place in an Erlenmeyer/Conical flask. Fill the flask with the oil bath. Place the PVC samples in the flask and seal using an appropriately sized rubber stopper. The rubber stopper should have two airlock holes to feed in two test tubes respectively. Make sure the flask is placed onto a heat source. Prepare a water bath within a large beaker and seal the beaker with an appropriately sized rubber stopper. This rubber stopper should also contain two airlock holes to place two respective test tubes. Connect one side of a test tube to a source of pressurized Argon gas, connect the other side of the test tube into the flasks first airlock hole. Connect another test tube from the flasks second airlock hole to the beakers first airlock hole. Connect another test tube from the beakers second airlock hole to a titration device. The titration device should utilize NaOH. Begin pumping nonreactive Argon gas throughout the apparatus to ensure all air is evacuated. The reaction apparatus is shown in the figure below:

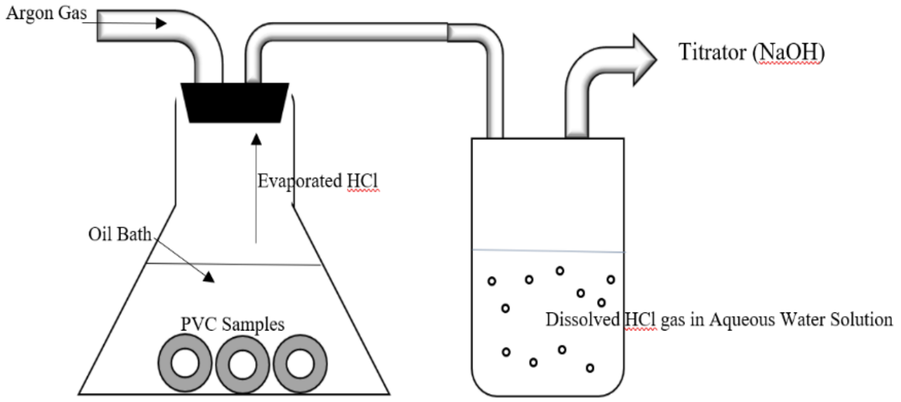


Figure 2

Experimental Procedure

Once the apparatus is prepared, the experiment may begin. It is important to note that various temperatures will be tested, thus, the experimental procedure will be repeated for each variation in temperature.

1. Heat the Flask initially at temperature T_1.
2. Begin pumping Argon gas through the rubber stopper into the Erlenmeyer flask.
3. As the reaction proceeds, titrate the aqueous HCl solution.
4. Measure the concentration of HCl produced over time.
5. For temperatures T_2, T_3, T_4, T_5, repeat steps 1-4.

Argon gas is used to push HCl gas from the flask into the water bath solution where it will dissolve. In an aqueous solution, HCl concentration can easily be determined using a titrating device. With the concentration of HCl determined over time, the overall rate of reaction can be determined.

Data Analysis

For each temperature T_1, T_2, T_3, T_4, T_5 the concentration of HCl [HCl] produced vs time will be determined. PVC thermal degradation is a first order reaction such that the ln[HCl] vs time will display the slope of -k as shown by the equation: $\ln[HCl]_t = -kt + ln[HCl]_0$

This is a logarithmic linearization of the integrated first order rate law:

$$[HCl]_t = [HCl]_0 e^{-kt}$$

Where:

$[A]_t$= Concentration at time T

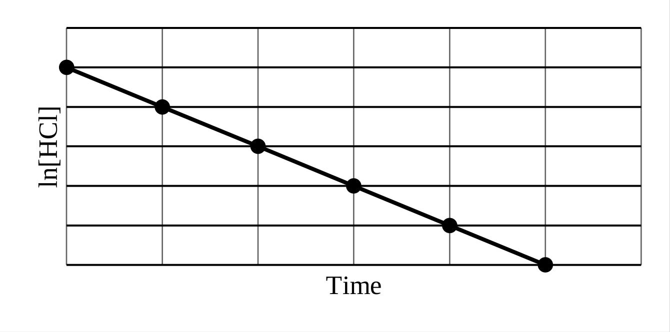
$[A]_0$= Initial concentration

e = Euler's number

k = Rate constant

t = Temperature

An example of an ln[HCl] graph vs time (t) at a certain temperature T is shown below.



Rate constants at various temperatures can be tabulated as follows.

Temperature	Rate Constant
T_1	K_1
T_2	K_2
T_3	K_3
T_4	K_4
T_5	K_5

After organizing the data, the values at various temperatures can be plugged in to the Arrhenius equation. The activation energy can be determined after graphing the linearized version of the equation:

$$\ln(k) = (\frac{1}{T})\frac{-E_a}{R} + \ln(A)$$

The new linear equation takes the form y=mx+b and can be graphed.

Where:

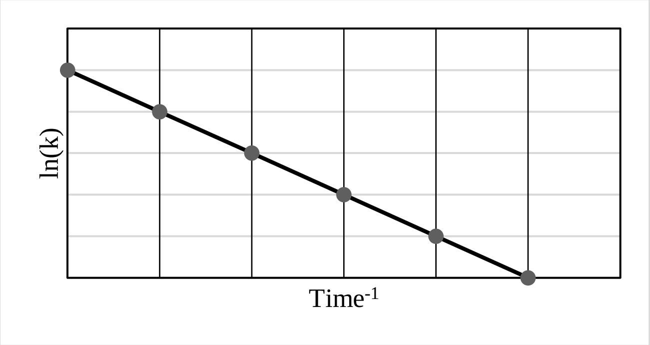
$\ln(k)$ = y

$\frac{-E_a}{R}$ = Slope “m”

$\left(\frac{1}{T}\right)$ = x

$\ln(A)$ = b

An example of the graph of ln(k) v t^{-1} is displayed below:



The graphically determined activation energy can then be used to relate rate constants at varying temperatures using the following equation:

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

Where,

k_2 = Reaction Rate Constant at Low Temperature (T_1)

k_1 = Reaction Rate Constant at High Temperature (T_2)

E_a = Activation Energy

R = Universal Gas Constant

T_2 = Low Temperature Value

T_1 = High Temperature Value

With the newly determined rate constant, the service-lifetime of PVC material can be estimated at varying temperatures.

Summary

The degradation of PVC occurs in three stages: low temperature moderation of degradation, medium temperature acceleration of degradation, high temperature moderation of degradation. It was shown that the atmosphere played a major role in the degradation of PVC. With the presence and variation of oxygen, nitrogen, hydrogen and water vapor levels impacting reactions. Additives can greatly reduce the release of HCl, meaning, they can lower the rate of reaction significantly. These include plasticizers, stabilizers, flame retardants and colorants.

- PVC decomposes at 140 degrees Celsius, melting temperature of 160 degrees Celsius.
- Coefficient of thermal expansion: $3x10^{-5}$ in/in/F
- Stabilizers are used to decrease the presence of structural imperfections in PVC that can cause, or initiate, dehydrochlorination reactions.
- The addition of plasticizers to PVC can change its structural resilience. They can make the PVC more flexible under high temperatures, and they can reduce the amount of discoloration during degradation.

Following the determination of activation energy of the PVC samples, one can determine various properties of the material. For instance, the amount and length of high temperature exposure the material can withstand can be determined. This is because the activation energy allows one to determine the amount of energy required to initiate the thermal degradation. With a calculated activation energy, one can estimate the lifespan of PVC material at various temperatures.

A common preventative measure for thermal shielding and flame resistance occurs during the polymerization process. Copolymers, such as intumescent additives, can be employed to provide a thermal layer between the heat susceptible plastic component and the heat source [2]. Many other methods include a topical finish which, like the integrated copolymers, act as a thermal barrier for the material [1].

Another common form of PVC being widely manufactured is chlorinated polyvinyl chloride (CPVC). This material can handle significantly higher temperatures than PVC. For any application requiring temperatures above PVC’s peak threshold, CPVC is recommended. These benefits come at an increased cost of production [3].

If a similar experiment were to take place with thermally resistant PVC samples, the reaction rate would be lower. This would result in a decreased rate constant, indicating an increased activation energy. It can be assumed that upon the addition of stabilizers to PVC, activation energy will increase [2].

Factors which reduce activation energy commonly include catalysts. However, catalysts function mainly in biological systems and do not apply to manufactured plastics per se. In the case of PVC, a factor which can significantly reduce activation energy is structural impurities at the molecular level [1]. The reaction mechanism by which PVC degrades is highly dependent on structural faults within the polymer. Bonds near these structural imperfections tend to split, causing a chain reaction which initiates the degradation. Low quality PVC may be more susceptible to thermal degradation, as it does not contain a symmetrical polymer structure relative to higher quality materials.

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