

Measurement of Arrhenius Parameters of the Second-Order Decomposition of Ethanal (CH₃CHO)

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Abstract: The Arrhenius parameter of the second-order decomposition of 2.5M ethanal was determined at different temperatures (700, 760, 810, 910K). The amounts of the ethanal remaining at specific time intervals were monitored with GC – MS and the values of rate constant K evaluated. From the graph of $\ln K$ vs $1/T$ plotted the activation energy, E_a for the decomposition was determined to be 189KJmol^{-1} and Arrhenius constant gave $1.1 \times 10^{12}\text{dm}^3\text{mol}^{-1}$. This implies that the thermal decomposition of acetaldehyde (ethanal) is strongly dependent on temperature.

Keywords: Arrhenius parameter, rate constant, activation energy, thermal decomposition

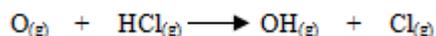
1. Introduction

It is almost axiomatic that the rates of chemical reactions increase with increasing temperature. For instance fuels such as gas, oil and coal are relatively inert at room temperature but burn rapidly at elevated temperatures. Many foods would last almost indefinitely when stored in a freezer but spoil quickly at room temperature. Metallic magnesium is inert in cold water but reacts with hot water. As a rule of thumb, reaction rates tend to double when the temperature is increased by 10°C [1].

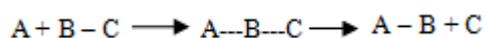
To understand why reaction rates depend on temperature we need a picture of how reactions take place. According to the **collision theory** model, a bimolecular reaction occurs when two properly oriented reactant molecules come together in a sufficiently energetic collision. To be specific, let's consider one of the simplest possible reactions, the reaction of an atom A with a diatomic molecule BC to give a diatomic molecule AB and an atom C:



An example of such reaction is that of an oxygen atom with an HCl molecule to give an OH molecule and a chlorine atom in atmospheric chemistry [2]:

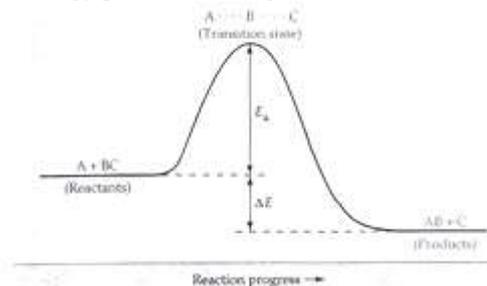


If the reaction occurs in a single step, the electron distribution about the three nuclei must change in the course of the collision such that a new bond, A – B, develops at the same time the old bond, B – C, breaks. Between the reactant and product stages, the nuclei pass through a configuration in which all three atoms are weakly linked together. We can picture the progress of the reaction as:



Now, if A and BC have filled shells of electrons (no unpaired electrons or vacant, low-energy orbitals), they will repel each other. To achieve the configuration A---B---C, then the atom requires energy to overcome this repulsion. The energy comes from the kinetic energy of the colliding particles and is converted to potential energy in A---B---C.

In fact, A---B---C has more potential energy than either the reactants or the products. Therefore, there is a potential energy barrier that must be surmounted before reactants can be converted to products, as depicted graphically on the potential energy profile in the figure below [2, 3]:



The height of the barrier is called **activation energy**, E_a , and the configuration of atoms at the maximum in the potential energy profile is called the **transition state**, or the **activation complex**. Since energy is conserved in the collision, all the energy needed to climb the potential energy hill must come from the kinetic energy of the colliding molecules. If the collision energy is less than E_a , the reactant molecules cannot surmount the barrier and they simply bounce apart. But, if the collision energy is at least as great as E_a , the reactants can climb over the barrier and be converted to products [4].

Experimental evidence has shown that very few collisions are productive because very few occur with a collision energy as large as the activation energy. The fraction of collisions with an energy equal to or greater than the activation energy E_a depends on temperature of the reacting system. This fraction f is approximated by the equation:

$$f = e^{-E_a/RT}$$

The fraction of collision having proper orientation for conversion of reactants to products is called the **steric factor**, p . For the reaction, $A + BC \rightarrow AB + C$, the value of p is expected to be about 0.5 because A has a nearly 50:50 probability of colliding with each of B and C ends of BC. For reactions of complex molecules, p is a fraction considerably less than 0.5 [1, 5].

The reaction is related also to the collision frequency, Z. So, considering all these parameters (fraction with required energy, f, steric factor, p and collision frequency, Z), the rate constant can be stated to be:

$$k = pZe^{-E_a/RT}$$

where k = rate constant, p = fraction of collision with proper orientation, Z = constant related to collision frequency, $e^{-E_a/RT}$ = fraction of collisions with sufficient energy for reaction, E_a = activation energy, T = temperature (K), R = universal gas constant. The above equation is usually written in a form called the **Arrhenius equation**, named after Svante Arrhenius, the Swedish chemist who proposed it in 1889 on the basis of experimental studies of reaction rates:

$$\text{Arrhenius equation: } k = Ae^{-E_a/RT}$$

The parameter A (=pZ) is called the **frequency factor** (or pre-exponential factor) [2].

2. Materials and Methods

The ethanal (2.5M) was allowed to decompose at the various temperatures (427, 487, 537 and 637°C) in a flask connected to GC –MS so that the amount of ethanal that reacted could be monitored over time. The amount of ethanal remaining was then used to calculate the rate constant k, at the varying temperatures. The Arrhenius parameters were then determined from the graph of $\ln k$ vs $1/T$.

3. Results and Discussion

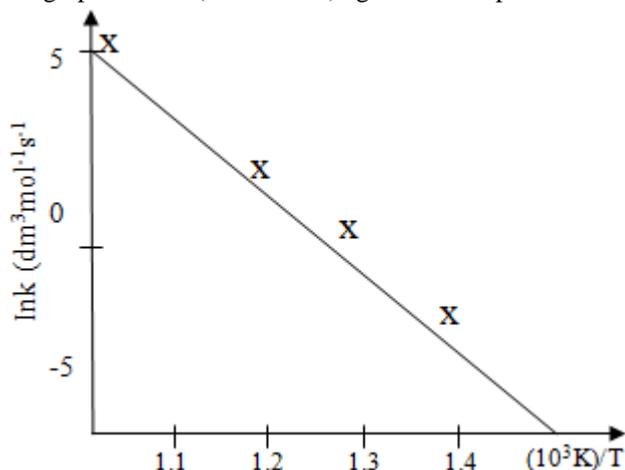
The amount of ethanal remaining and time for the decomposition at the stipulated temperatures are presented in the table below:

[CH ₃ CHO]:	2.1	1.8	1.3	0.9
t(s)	410	325	286	241
T(k)	700	760	810	910

Being a second-order reaction, the values of rate constant were evaluated thus:

$$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1}): 0.011 \quad 0.105 \quad 0.789 \quad 20.0$$

The graph of $\ln k$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$) against $1/T$ is plotted



From the graph;

The slope = - 22.7 and intercept = 27.7. Therefore, the activation energy, $E_a = 22.7 \times (8.3145\text{JK}^{-1}\text{mol}^{-1}) \times 10^3\text{K} = 189\text{kJmol}^{-1}$. $A = e^{27.7}\text{dm}^3\text{mol}^{-1}\text{s}^{-1} = 1.1 \times 10^{12}\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$.

The fact that the E_a is given by the slope of the plot of $\ln k$ against $1/T$ means that, the higher the activation energy, the stronger the temperature dependence on the rate constant (i.e., the steeper the slope). A high activation energy signifies that the rate constant depends strongly on temperature. Therefore, it can be said that the thermal decomposition of acetaldehyde (ethanal) is strongly dependent on temperature.

We can also conclude that for a reaction involving collision of molecules as in the decomposition of ethanal described in this research, the activation energy is the minimum kinetic energy that the reactants must have in order to form products. For instance, in a gas-phase reaction we are discussing, there are numerous collisions each second, but only tiny proportions are sufficiently energetic to lead to reaction. The fraction of collisions with a kinetic energy in excess of an energy E_a is given by the Boltzmann distribution as $e^{-E_a/RT}$.

References

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