

Determination Of Activation Energy For The Catalytic Oxidation Of Toluene To Benzaldehyde Using Chromium (Vi) Oxide/Hydrogen Peroxide Oxidant System

¹ABDU M.S., ²ASKA, A.S., ³FARUQ U.Z., ⁴DANGOGGO S.M., and ⁵ALI A.U
^{1&2}Department of Chemistry, Aminu Saleh College of Education Azare- Bauchi State, Nigeria
^{3,4&5}Department of Pure and Applied Chemistry, Usmanu Danfodio University Sokoto, Nigeria.

Abstract: Chemical kinetics is a branch of physical chemistry which is concerned with the study of the rates of chemical reactions and with the elucidation of the mechanism by which they proceed. Activation energy is an important parameter in kinetics whose knowledge assists one in determining the optimum energy requirement for the target reaction. The rate of the reaction was measured by monitoring the rate of disappearance of Toluene from the reaction mixture at various time intervals using UV/Vis spectrophotometer at 259nm (λ max). The experiment was carried out at 30°C and then repeated at 35°C, 40°C, 45°C and 50°C. From the various absorbance generated at these temperatures, the values of specific rate constants (k) calculated using first order equation were 1.0×10^{-3} , 2.20×10^{-3} , 3.0×10^{-3} , 4.5×10^{-3} and 6.1×10^{-3} respectively. The activation energy was determined from the plot of Natural log of specific rate constant ($\ln k$) against the reciprocal of temperature. From the plot, the activation energy was found to be 89.635KJ/mol.

Keywords: Determination, Activation energy, Toluene, Catalytic oxidation, Benzaldehyde.

Date of Submission: 21-07-2017

Date of acceptance: 28-09-2017

I. Introduction

Toluene is found naturally in petroleum but is mostly produce in some petroleum refining processes. It is used as octane enhancer in gasoline and as solvents for paints, rubbers, adhesives etc. toluene is also used as a petrochemical precursor in the production of toluene diisocyanate (TDI), benzaldehyde and benzoic acid. Benzaldehyde is the most industrially useful member of aromatic aldehydes (India petroleum industry, 2011). It is liquid at room temperature, denser than water and in fact insoluble in it. Benzaldehyde however exists in nature mostly in glycosidic form in almond, apricot, cherry and peach seeds. It is chiefly used as a precursor to other organic compounds ranging from pharmaceuticals to plastic additives. It is also used in the manufacture of dyes, cinnamic acid, perfumes and flavouring agents (Antejukic, 2013). A lot of literature indicated that toluene cannot be oxidized to benzaldehyde even under suitable temperature, concentration and reaction time without the application of a catalyst. Catalysts are substances that change the rate at which a chemical reaction approaches equilibrium without them becoming permanently involve in the reaction. They include first transition metal series and their oxides (Ti, Cr, Mn, Fe, Co, CuO, CrO₃, Fe₂O₃, V₂O₅ (Cotton, *et al.*, 1999). When carbon atom, in an organic compound loses a bond to hydrogen or gains a new bond to a heteroatom (or to another carbon) then the compound is said to be oxidized. Chemical kinetics also known as reaction kinetics is concerned with the study of the rates of chemical reactions and with the elucidation of the mechanism by which they proceed. Besides, information about the speed at which reaction occurs, Kinetics also sheds light on the reaction mechanism i.e. exactly how the reaction occurs. The knowledge of chemical kinetics will enable one to determine kinetic parameters of a specific reaction. The kinetic parameters include the order of reaction, specific rate constant and activation energy (Petrucci *et al.* , 2007).

Activation energy (E_a) is the minimum energy required to initiate a chemical reaction. If the energy of the reacting species is lower than the E_a the reaction may not be feasible, On the other hand, if the energy of the reacting species is higher than activation energy the reaction is feasible but with the formation of side products. Oxidation of toluene to benzaldehyde without catalyst indicated that the energy of toluene and the oxidant is lower than the activation energy. Therefore, this work is designed to determine the E_a of catalytic oxidation of toluene to benzaldehyde.

II. Methodology

Materials: Spectrophotometer (722-2000), water bath (TU-160), thermometer, weighing balance (Ar3130).
Samples: Chromium(VI)Oxide(CrO₃),HydrogenPeroxide(H₂O₂),Toluene(C₆H₅CH₃),
Acetone(CH₃COCH₃),Distilledwater,Iron(III)Sulphateheptahydrate(Fe₂(SO₄)₃.7H₂O).

Determination Of Activation Energy Of Toluene Oxidation

The procedure for the determination of the rate of disappearance of toluene from the reaction mixture was adopted from the method described by Petrucci *et al.*, 2007. Ten milligrams (10mg) of CrO₃ was weighed and transferred into 100cm³ conical flask followed by 5mg of a catalyst [Fe₂(SO₄)₃.7H₂O], 20cm³ of acetone/water (1:1) and 2cm³ of toluene. The conical flask was placed in a vibrating water bath set at 30°C and allowed to equilibrate. The flask was then stoppered with an air-tight cork and 20cm³ of H₂O₂ was introduced using hypodermic syringe through the cork and the content was shaken continuously for 10minutes. The rate of disappearance of the toluene was monitored by withdrawing 4cm³ of the content every 10 seconds and its absorbance on UV/Vis. Spectrophotometer at 259nm wavelength. The procedure was repeated at 35, 40, 45 and 50°C. The data was used to determine the rate constant and then the activation energy.

III. Results

TABLE 1 Data values obtained from Toluene oxidation at 30°C

Time (sec)	A ₀	lnA ₀	A	lnA	K (specific rate constant)
0	1.537	0.430	-	-	-
4	-	-	1.53	0.428	1.0 x 10 ⁻³
6	-	-	1.52	0.422	1.0 x 10 ⁻³
8	-	-	1.51	0.412	1.0 x 10 ⁻³
10	-	-	1.50	0.402	1.0 x 10 ⁻³

Table 2 Data values obtained from Toluene oxidation at 35°C

Time(sec)	A ₀	lnA ₀	A	lnA	K (specific rate constant)
0	1.649	0.50	-	-	-
4	-	-	1.64	0.495	2.20 x 10 ⁻³
6	-	-	1.63	0.493	2.20 x 10 ⁻³
8	-	-	1.62	0.482	2.20 x 10 ⁻³
10	-	-	1.61	0.481	2.20 x 10 ⁻³

Table 3 Data values obtained from Toluene oxidation at 40°C

Time(sec)	A ₀	lnA ₀	A	lnA	K (specific rate constant)
0	1.768	0.57	-	-	-
4	-	-	1.760	0.563	3.0 x 10 ⁻³
6	-	-	1.750	0.559	3.0 x 10 ⁻³
8	-	-	1.740	0.556	3.0 x 10 ⁻³
10	-	-	1.730	0.553	3.0 x 10 ⁻³

Table 4 Data values obtained from Toluene oxidation at 45°C

Time(sec)	A ₀	lnA ₀	A	lnA	K (specific rate constant)
0	1.869	0.640	-	-	-
4	-	-	1.870	0.628	4.5 x 10 ⁻³
6	-	-	1.860	0.623	4.5 x 10 ⁻³
8	-	-	1.850	0.617	4.5 x 10 ⁻³
10	-	-	1.840	0.612	4.5 x 10 ⁻³

Table 5 Data values obtained from Toluene oxidation at 50°C

Time(sec)	A ₀	lnA ₀	A	lnA	K (specific rate constant)
0	2.034	0.710	-	-	-
4	-	-	2.000	0.692	6.1 x 10 ⁻³
6	-	-	1.960	0.684	6.1 x 10 ⁻³
8	-	-	1.955	0.676	6.1 x 10 ⁻³
10	-	-	1.931	0.658	6.1 x 10 ⁻³

Key: A₀ = initial concentration, lnA₀ = Natural log of initial concentration

A= Concentration at various time intervals, lnA= Natural log of concentrations at various time intervals, K= Specific Rate Constant

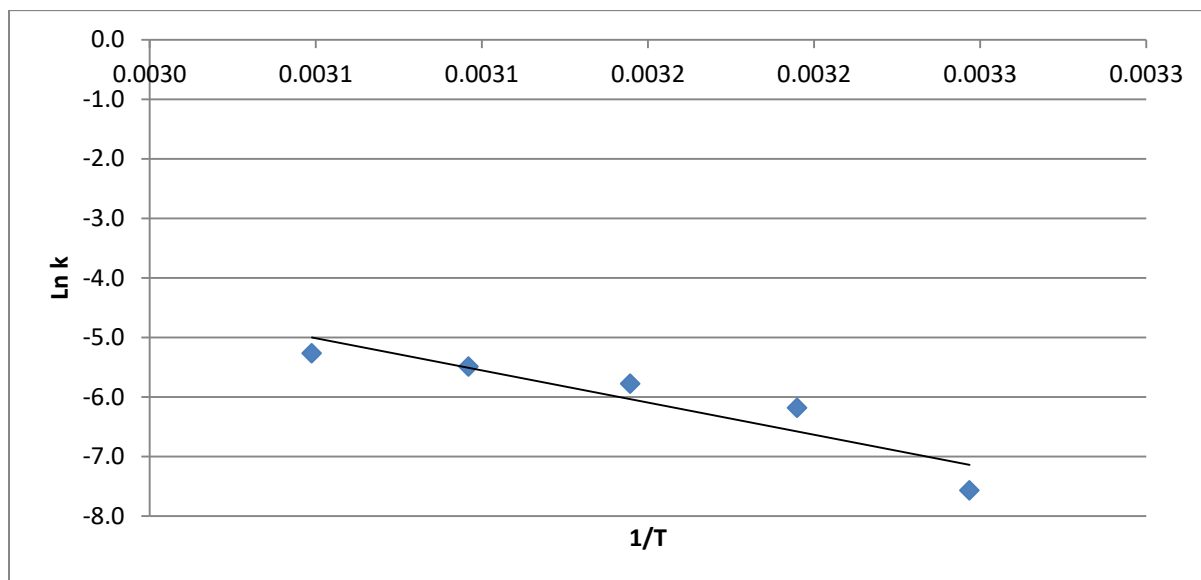


Fig. 1 Arrhenius Plot for determination of Activation Energy using $\ln k$ against reciprocal of temperature

IV. Discussion

In the procedure for the experiment to determine of rate of reaction of toluene, it can be seen that acetone/ water medium was used. This was necessitated by the fact that toluene is not miscible with water. Thus acetone was used to solubilize toluene. The choice of acetone was informed from the fact that it is sufficiently inert to the oxidation by H_2O_2 or more correctly by oxygen because it does not have any active oxygen (Wang *et al.*, 2005). Furthermore, it is miscible with both water and toluene hence it is capable of bringing the toluene into the reaction medium without itself participating in the reaction.

In this experiment, the rate of disappearance of toluene was monitored on UV spectrometer using its λ_{max} . The experiment was carried out at 30°C. In order to determine the activation energy, the experiment was repeated at 35, 40, 45 and 50°C then the corresponding specific rate constants were calculated from the data generated as shown in tables 1-5 above.

Activation energy, knowledge of which helps in determining the optimum energy requirement for the target reaction (i.e. Benzaldehyde from the catalytic oxidation of toluene) was determined from the plot of $\ln k$ against $1/T$ (fig. 1). From the slope of the graph, the activation energy was calculated using the following equation, i.e. Slope = $-E_a/R$ where, E_a is activation energy, R is the gas constant (8.314J/mol)(Anslyn and Dougherty, 2007).

Activation energy is very important in kinetics, because any energy input lower than it would fall short in producing the right product. Likewise excess energy may result in another unwanted product. Since the feasibility of a reaction rests on the value of activation energy, in this catalytic oxidation of toluene which proceeded in accordance with Arrhenius equation the value of activation energy was found to be 89.635KJ/mol. This value is sufficient enough for the reacting species to surmount the activation complex and produce the required products.

Acknowledgement

The Authors wish to acknowledge the management of Aminu Saleh College of Education, Azare Bauchi State for providing us with an equipped laboratory. We also wish to acknowledge the academic contributions of Professor U. Z. Farouq Prof. S.M. DANGOGGO and Prof. A.U. ALI of Usmanu Danfodiyo University Sokoto, Nigeria. The contributions of Lab. Technician Malam Ibrahim Shira and Lab. Assistants Ibrahim Musa and Nura Musa of Chemistry Lab., Aminu Saleh College of Education, Azare cannot be overemphasized.

References

- [1]. Anslyn E. V. and Dougherty D. A. (2007): Discussion of reaction kinetics and their application to organic chemistry: Modern physical Organic chemistry. University Science Books: Sausalito, 2006; p. 27.
- [2]. Antejukic, (2013): Crude oil: Composition, Classification, Coal; Oil Shale; Tarsand; Gas Hydrates: Petroleum Refining and Petrochemical processes, Zavodza Technologiju Nafto, Petrokeniju Her-10000 Zagreb, Sauska Cesta 16 p 177.
- [3]. Cotton, F.A; Wilkinson, G., Muriko, C.A. and Bochmann, M.(1999): Advanced inorganic chemistry, John Wiley p. 457-775.
- [4]. India Petroleum industry, 2011: Multifacet uses of petrochemicals. 2011 (online) (18/12/2016). Available from Worldwide web.

- [5]. Petrucci, R. H., William S. H., Geoffrey, H. and Jiffy D. M. (2007): Chemical kinetic, General Chemistry Principles and modern application. 9th Edition, Upper Saddle River, N J Person Edu. 2007.
- [6]. Wang, J. Xiaoqiongli, J., Lipeng, Z. and Ryuichiro, O. (2005): Liquid phase oxidation of Toluene to Benzaldehyde with Molecular Oxygen Over Copper Based Heterogenous Catalysis, Advanced Synthesis and Catalysis, Vol. 347 No. 15 Pp. 1987-1992.

ABDU M.S. "Determination Of Activation Energy For The Catalytic Oxidation Of Toluene To Benzaldehyde Using Chromium (Vi) Oxide/Hydrogen Peroxide Oxidant System." IOSR Journal of Applied Chemistry (IOSR-JAC) , vol. 10, no. 9, 2017, pp. 28–31.