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Research Article

A Comparative Study of Kinetics of Oxidation of Isoamyl Alcohol and Isobutyl Alcohol by Acidic Permanganate

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Abstract

A Kinetic investigation of oxidation of isoamyl alcohol and isobutyl alcohol by acidic permanganate in presence of surfactant as catalyst has been carried out spectrophotometrically. The reaction is double stage process in which first stage is followed by second fast stage process. The rate shows a first order dependence on each oxidant and substrate. The reaction is studied at different temperatures to evaluate usual kinetic parameters such as rate constant.

Keywords: Surfactant, Catalysis, Rate constant, Kinetic parameters, Oxidation, Spectrophotometer.

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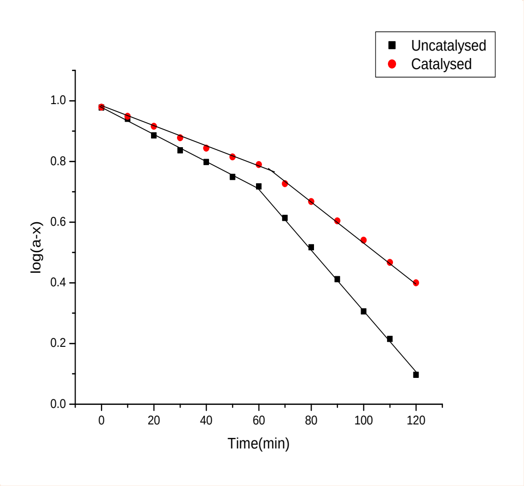
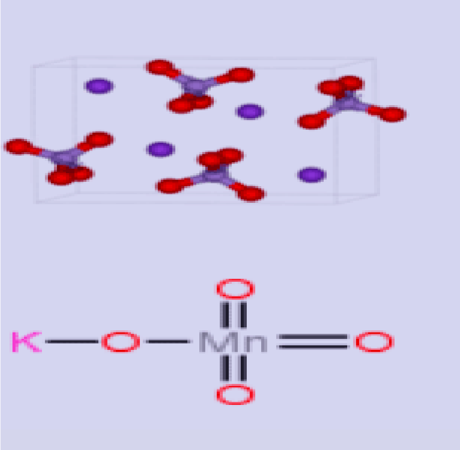
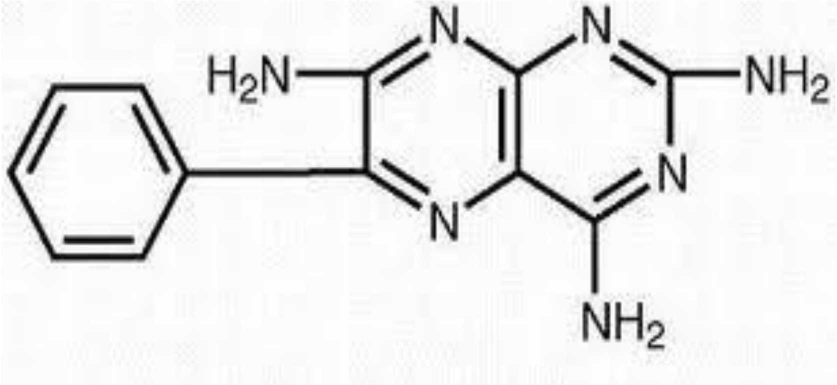


Introduction

Comparison of isoamyl & isobutyl alcohol has been performed spectrophotometrically and kinetics of the reaction has been investigated. In this experiment oxidation of alcohols is done by oxidizing agent. Any oxidizing agent can be used but here permanganate ion is used. An oxidizing agent (also oxidant, oxidizer or oxidiser) is the element or compound in an oxidation-reduction (redox) reaction that accepts an electron from another species. Because the oxidizing agent is gaining electrons (and is thus often called an electron acceptor), it is said to have been reduced. The oxidizing agent is $KMnO_4$. It is a salt consisting of K^+ and MnO^{-4} ions. Formerly known as permanganate of potash or Condy's crystals, it is a strong oxidizing agent. It dissolves in water to give intensely pink or purple solutions. Its structure is shown below:

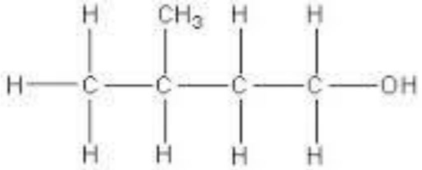


A substrate is a molecule upon which an enzyme acts. Enzymes catalyze chemical reactions involving the substrate. In this reaction substrate is iso amyl & iso butyl alcohol. The enzyme used in this reaction is NaLS. Sodium laureth sulfate, or sodium lauryl ether sulfate (SLES), is an anionic detergent and surfactant. Its chemical formula is CH_3 $(CH_2)10CH_2$ (OCH_2CH_2) $nOSO_3Na$. Sometimes the number represented by n is specified in the name, for example laureth-2 sulfate. The product is heterogeneous in the number of ethoxyl groups, where n is the mean.



The substrate used in this experiment is iso amyl alcohol & iso butyl alcohol. Let us discuss some properties of both of them.

Isoamyl alcohol (also known as isopentyl alcohol) is a clear, colorless alcohol with the formula (CH3)2CHCH2CH2OH. Colorless liquid with a mild, choking alcohol odor. Less dense than water, soluble in water. Hence floats on water. It produces an irritating vapor.



3-methyl-1-butanol
(isoamyl alcohol)
$C_5H_{12}O$

Very high vapor concentrations irritate eyes and upper respiratory tract. Continued contact with skin may cause irritation. Isobutanol (IUPAC nomenclature: 2-methylpropan-1-ol) is an organic compound with the formula (CH3)2CHCH2OH. This colorless, flammable liquid with a characteristic smell is mainly used as a solvent. Its isomers include n-butanol, 2-butanol, and tert-butanol, all of which are important industrially.

All the reagents used in this experiment is of AR grade. The experiment was carried out in thermostat at controlled temperature. The total volume of reaction mixture was kept 100ml.

The oxidation of Poly Vinyl Alcohol by permanganate ion in perchlorate solution was studied by Ishaaq.A.Jaffrany[1],Kinetics studies in the surfactant catalyzed oxidative deamination & decarboxylation of glycine by acidic permanganate explored by N.Bende et.al.[2], Kinetic studies in the surfactant catalyzed oxidative deamination and decarboxylation of L-Valine by permanganate in sulphuric acid medium observed by Bende and coworkers[3].

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K.Bijudas & T.D. Radhakrishnan Nair[5], Oxidation by Permangnate: synthetic & mechanistic aspects researched by Sukalyan Dash & coworkers[6].

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Experimental

Material and Method

All the reagents used in this experiment are of AR grade. The experiment was carried out in thermostat at controlled temperature. The total volume of reaction mixture was kept 100ml.

The kinetics of oxidative decarboxylation of iso-amyl alcohol and iso-butyl alcohol by acidic permanganate in the presence of surfactant (Sodium Lauryl Sulphate - NaLS) has been reported. For finding out the kinetic parameters, the Ostwald's Isolation method was applied[31]. Requisite amount of the solutions of iso-amyl alcohol and iso-butyl alcohol, Surfactant (NaLS), Perchloric Acid and water (to maintain the total volume constant for all the runs) were taken in black pained glass stopper bottles to avoid any photochemical effect from outside and were thermo stated (of ±0.1^{o}C accuracy) at constant required temperature. A measured amount of permanganate solution at the same temperature was added to the reaction mixture. The reaction mixture was then shaken well. The zero time of the reaction was noted when half of the permanganate solution was added. 2ml of the reaction mixture was withdrawn at known intervals of the time and the reaction was quenched by adding it into known excess of ice cold water in the optical cell. The progress of the reaction was measured in terms of the absorbance spectrophotometrically at 515nm band on chemiline digital CL 320 Spectrophotometer. The reactions were studied almost upto 60-80% completion.

Result and Discussion

Nature of Reaction The oxidation of alcohols has been investigated by various scientists to study the reaction rates. As I performed it on iso-amyl alcohol and iso-butyl alcohol it was observed that the reaction is double stage process i.e. first slow reaction followed by fast reaction. The kinetics studies suggest that the reaction is first order. The reaction is studied till completion when the color of the permanganate ion disappears from the reaction mixture. The typical run of both the alcohol in presence and absence of surfactant at 35^{oC} is attached below: (**Figure 1 and 2**)

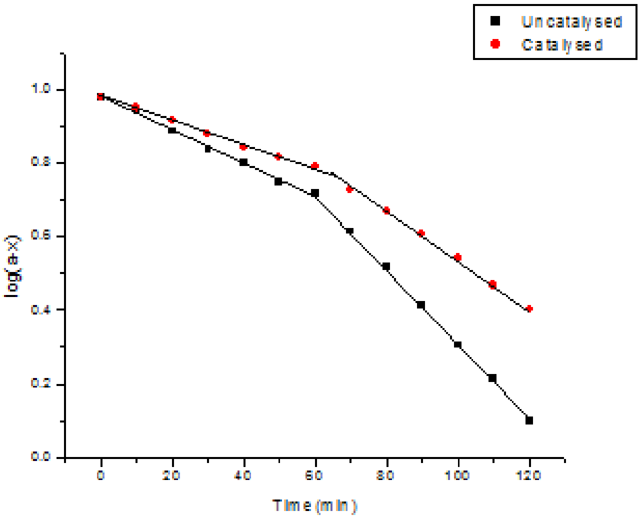

Figure 1 Typical Run of isoamyl alcohol

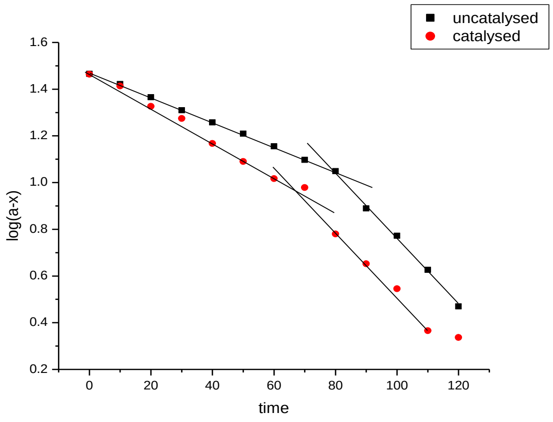

Figure 2 Typical Run of Isobutyl Alcohol

Variation Of Surfactant(NaLS)

The surfactant used in the reaction is NaLS which increase the rate of reaction by micellar catalysis. The variation of surfactant extensively studied on both the substrates i.e. isoamyl alcohol & isobutyl alcohol. The NaLS added in the range of $1X10^{-4}M$ to $4X10^{-4}M$.It was found that although the reaction is first order but the concentration of surfactant greatly enhances the rate of oxidation. The values of k1 & $k_1^{'}$ for slow and fast process is shown in Table 1 & graphs between time and log(a-x) has been shown as Figure 3 & Figure 4 for both alcohols.

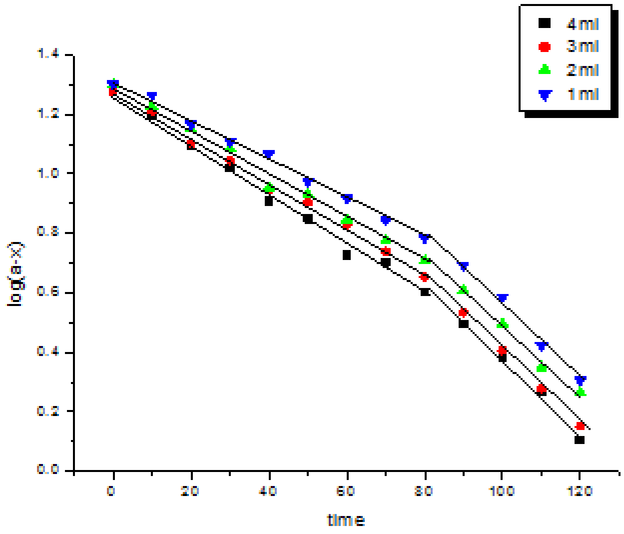

Figure 3 NaLS Variation on Iso Amyl Alcohol

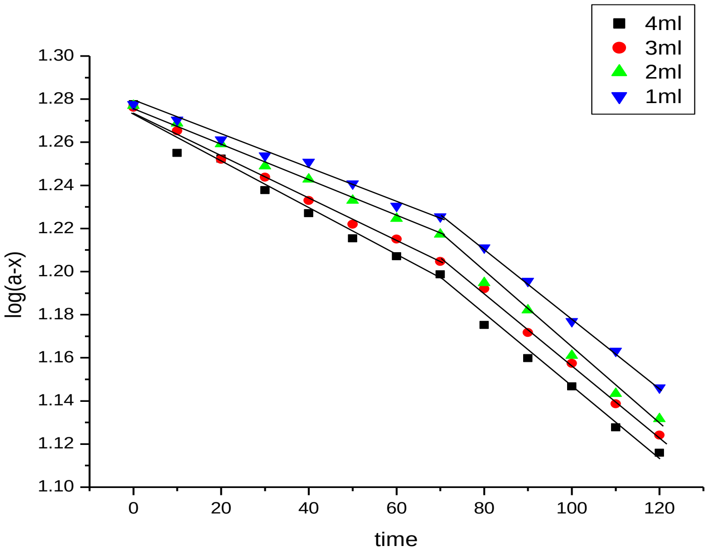

Figure 4 NaLS Variation on Isobutyl Alcohol

From the table it can be concluded that on increasing surfactant concentration the rate of the reaction increased as the values of k_1 & k_1' both, found to be enhanced by increasing NaLS.

Table 1 Variation Of Surfactant(NaLS)

[Substrate]= 0.05 N
Temp. = 35°C

[H_2SO_4] =3N
[$KMnO_4$] =1x10^{-3}N

[NaLS]M	**Isoamyl Alcohol**		**Isobutyl Alcohol**	
	k_1 X 10^{-3} min^{-1}	k_1' X 10^{-3} min^{-1}	k_1 X 10^{-3} min^{-1}	k_1' X 10^{-3} min^{-1}
1x10^{-4}	1.3825	2.6046	0.1977	0.4598
2x10^{-4}	1.7389	2.5037	0.2548	0.5430
3x10^{-4}	1.7759	2.8244	0.3032	0.4821
4x10^{-4}	1.9089	2.6015	0.3400	0.4850

Variation Of H_2SO_4 **(H^+)-** The variation of acidic media i.e. sulphuric acid has investigated in order to study its effect on the reaction rates. It was found that on increasing acidity of solution by increasing concentration of [H+], the rate of the reaction greatly increased. In both the substrates the reaction rates greatly enhanced. It is due to the protonation of the oxidant according with equilibrium

$$\mathbf{MnO4^- + H^+ \Leftrightarrow HMnO4}$$

Table 2 below shows the k and k' values for both the alcohols respectively; The graph between time and log(a-x) has been shown as Figure 5 and Figure 6 respectively.

[H^+]= 1x10^{-4} mole/dm^2
Temp. =35°C

[Substrate] = 0.05 N
[$KMnO_4$] = 1x10^{-3}N

Table 2 Variation Of H_2SO_4(H^+)

[H^+]M	Isoamyl Alcohol		Isobutyl Alcohol	
	k_1 X 10^{-3} min^{-1}	k_1' X 10^{-3} min^{-1}	k_1 X 10^{-3} min^{-1}	k_1' X10^{-3} min^{-1}
3×10-4(withoutNaLS)	1.2367	4.2057	0.1310	0.2943
3×10-4	1.5632	3.7515	0.1740	0.4251
3.5×10-4	1.7453	2.5393	0.2200	0.3586
4×10-4	2.0988	4.2129	0.2778	0.3738
4.5×10-4	2.2933	3.8061	0.3133	0.3569
5×10-4	2.4539	4.6068	0.34552	0.3811

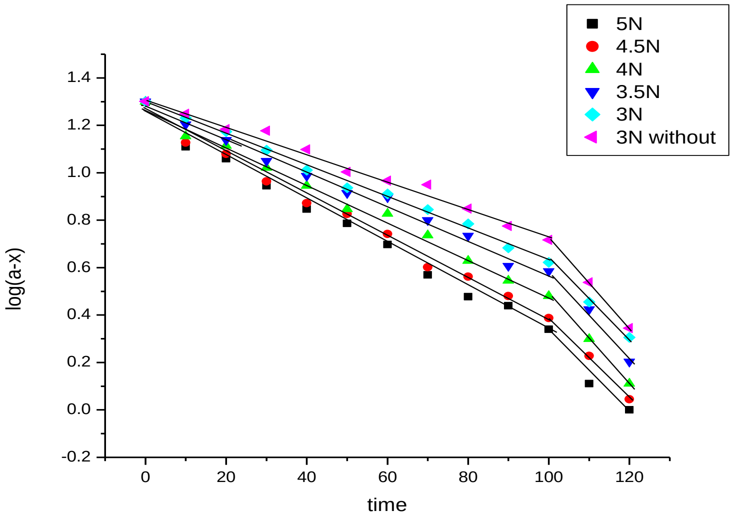

Figure 5 Acid Variations on Isoamyl Alcohol

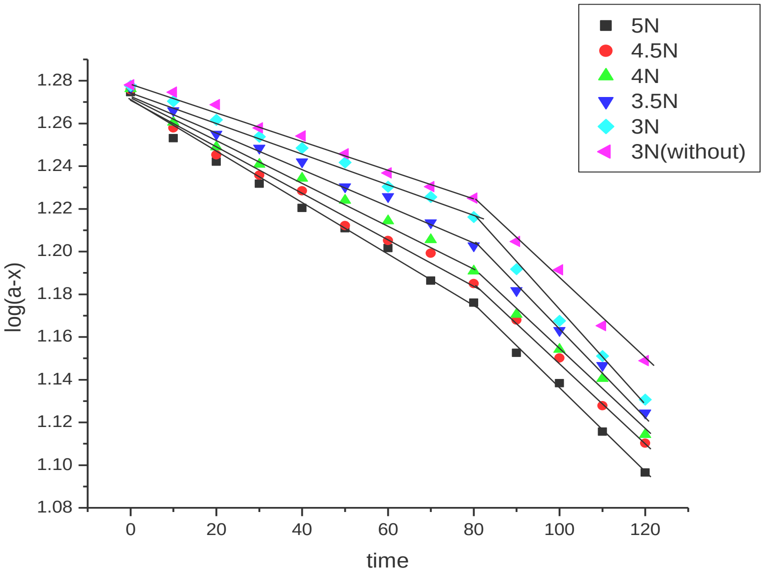

Figure 6 Acid Variations on Isobutyl Alcohol

Conclusion

The total order of reaction investigated found to be first order with respect to all the parameters. The variation of surfactant & H^+ performed in this experiment has no effect on order of the reaction inspite of the considerable effect of their concentration seen on the kinetics of the reaction.

The experiment has been performed on both isoamyl & isobutyl alcohol. From **Table 1** & **Table 2**, which gives the value of rate constant for both slow and fast process, it can be clearly observed that on both the alcohols the effect of varying concentration is same to increase the reaction rate. Both the H^+ & NaLS variation showed pronounced effect on isoamyl alcohol as compare to isobutyl alcohol, as the values suggest.

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