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Research Article

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Kinetics of iodination of acetone, catalyzed by HCl and H_2SO_4 - a colorimetric investigation of relative strength

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ABSTRACT

Iodine gives a deep yellowish brown color in aqueous solution. As acetone is iodinated and Iodine is converted to iodide ion, this color slowly fades as iodine is consumed. Thus iodination of acetone can be investigated by the change in absorbance. In the present investigation, kinetics of this reaction has been studied colorimetrically. The extent of the reaction has been monitored by measuring the absorbance in the visible region (λ_{max} = 470nm) There is a decrease in absorbance indicating the consumption of Iodine. H^+ ion acts as a catalyst in this reaction. Thus, the kinetics of iodination of acetone has been studied in presence of HCl and H_2SO_4 and the rates have been compared to determine their relative strength. An attempt has been made to reduce the consumption of chemicals to a very low level.

Keywords: Iodination, kinetics, colorimetric, absorbance, relative strength.

INTRODUCTION

Study of the Iodination reaction began in 19th century when it was noticed that yellow color of iodine slowly fades when the solution also contains acetone. Since then, reactions involving a reactant containing a central carbonyl group have become some of the popular organic chemical reactions. The iodination of acetone is also catalyzed by hydrogen ions. The effects of varying the concentrations of acetone, iodine and hydrogen ions have been studied earlier and it has been found that the reaction is zero order with respect to iodine.

The overall stoichiometric equation for the iodination is:-

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI \quad (1)$$

If this represented the mechanism of the reaction, the rate of reaction would be proportional to both the acetone and iodine concentrations. This proportionality is not found.

The following mechanism has been reported in the literature[1]

$$CH_3COCH_3 + H^+ \rightarrow CH_3.C(OH)=CH_2 + H^+ \quad (2)$$

$$CH_3.C(OH)=CH_2 + I_2 \rightarrow CH_3.CO.CH_2I + HI \quad (3)$$

Of these steps, (3) is rapid and without influence on the overall rate of iodination, while (2) - the enolisation of acetone - is slow and is the rate-determining step. In the presence of excess of acetone and at constant hydrogen ion

concentration, therefore, the iodination should proceed from start to finish at a constant rate. Thus rate of this reaction has been found to depend on the concentration of acid and acetone.

Study of kinetics of this reaction has been included in the undergraduate chemistry curriculum. The procedure involves titrating the mixture against standard Sodium thiosulphate using starch indicator to measure the amount of Iodine in the mixture [2]. However the presence of Iodine imparts color to the solution . The color fades with time as the reaction proceeds. Thus the reaction can be studied by colorimetry by measuring the absorbance after definite time intervals. The reaction occurs in the presence of acid as catalyst. This fact can be utilized to study different acids as catalyst to determine their relative strength. Generally, in undergraduate classes, relative strength of the two acids is determined by studying the hydrolysis of methyl acetate in presence of the two acids. But this is again a time consuming method involving titration of the mixture with standard NaOH after definite time intervals. [3] Also, it requires large amount of chemicals. Microscale experiments have been suggested earlier for teaching laboratory courses. [4,5]

Therefore in the present investigation, kinetics of iodination of acetone has been studied colorimetrically in presence of HCl and H_2SO_4 and compared. The extent of this reaction is monitored by measuring the absorbance at 470 nm.

Materials and Methodology:

The colorimetric investigation of this reaction comprised chemicals viz., Iodine and Acetone manufactured at Pune Chemical Laboratories (purified before use), HCl and H_2SO_4 were from A.V.Gandhi and Co.,Pune. Colorimeter EQ-650A was used for measurement of absorbance during reaction.

Primarily, the acids were standardized to exactly equal normalities. The normality of the acids was found to be 0.992 N. These solutions were stored in closed containers. Iodine solution was prepared by the procedure given in the literature.[6] Standard Iodine solution (0.1M) was stored in dark. It was diluted to 0.02M before introducing in the mixture. Freshly prepared 1M acetone was used for all the experiments.

λ_{max} was determined for Iodine using distilled water as reference. Kinetic studies were performed by noting the absorbance of a mixture of acetone, acid and Iodine. 1 ml of each solution was taken to get 3 ml of the reaction mixture. Thus, the reaction mixture contained ≅ 0.33 N acid (HCl), 0.33M acetone and 0.0066 M Iodine. The whole reaction mixture was taken in glass cuvette and absorbance of the mixture was noted at 470nm at definite time interval of 1 min. The procedure was repeated by replacing HCl by H_2SO_4.

A graph of Absorbance Vs Time was plotted for both the experiments and compared.

RESULTS AND DISCUSSION

A graph of Absorbance Vs Wavelength was plotted (Fig 1). λ_{max} was found to be 470nm. This filter was chosen for further experiments.

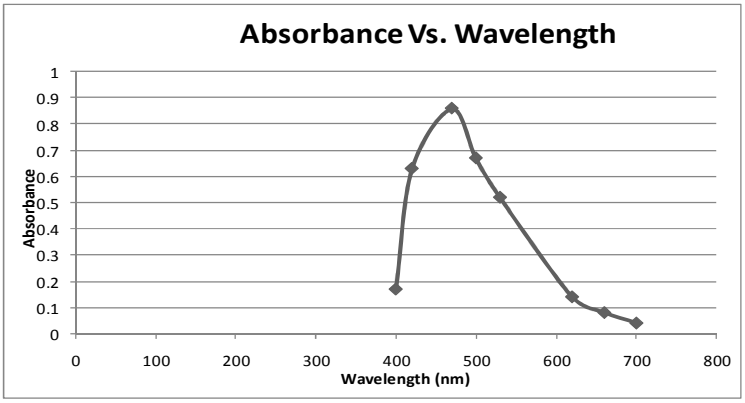

Fig.1: Absorbance vs. Wavelength

Kinetic studies show that the absorbance of a mixture containing acid, acetone and Iodine decreases with time and solution becomes colorless after a certain time. Absorbance decreases faster in presence of HCl than H_2SO_4. This observation was utilized to determine the relative strength of the acids. Absorbance of the mixture was measured at time interval of 1 min, till the absorbance attained a steady value. It was plotted against time in each case as shown in Fig 2 and 3.

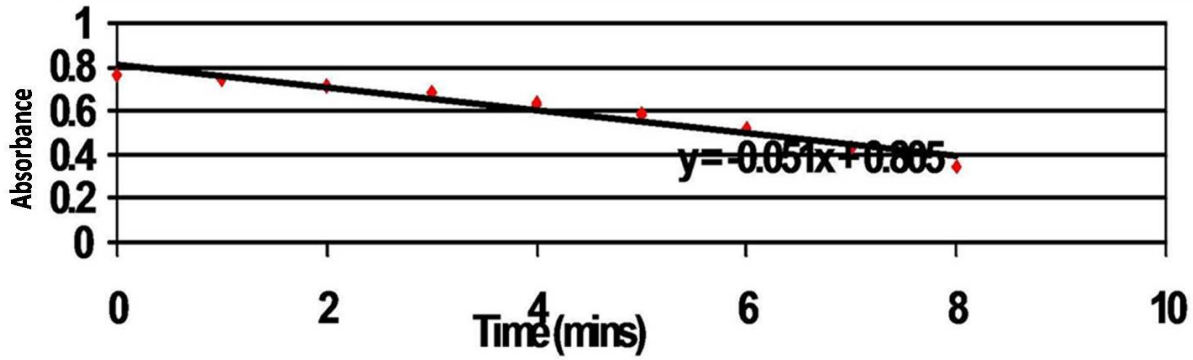

Fig. 2: Absorbance vs. time (in minutes) in presence of HCl

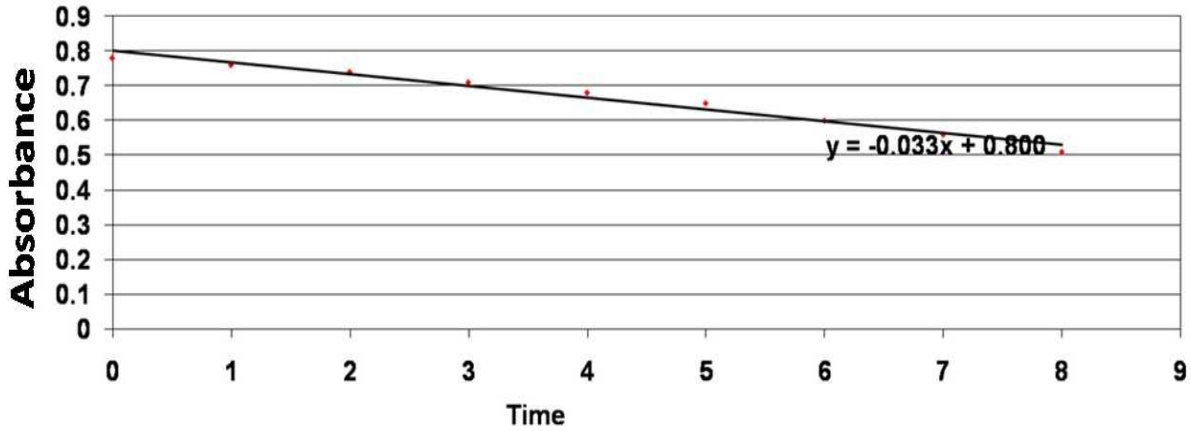

Fig. 3: Absorbance vs. time (in minutes) in presence of H_2SO_4

Comparing both the plots, it is observed that the plot for a mixture containing HCl is steeper having a slope of 0.051 whereas a mixture containing H_2SO_4 has a slope of 0.033. This shows that the rate of reaction is higher in presence of HCl. The ratio of the slopes has been found to be equal to 0.65 which gives the relative strength of the two acids.

Table 1: Comparison of titration and colorimetric method

	Titration method	**Colorimetric method**
Total volume of solution	100 ml	3 ml
Chemicals required	Acetone, Iodine, Acid, Sodium thiosulphate, sodium acetate, potassium iodide & starch indicator	Acetone, Iodine, Acid.
Manual errors	More likely	Negligible
Time intervals	3 min	1 min

Generally, titration method is used for studying this reaction. The volume of solutions required for the titration method is comparatively much more than those for the colorimetric method (Table 1). Also the amounts of chemicals used for the volumetric method exceed those used for colorimetric method. As most of the

experimentation in titration is mechanical, manual errors are more likely, but in colorimetric method as most of the experimentation is on the e-device, manual errors are minimized. The time intervals are also reduced to a greater extent and can be reduced further if needed.

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