

A Kinetic Study on the Determination of Hydrazine by Iodine in Sulphuric Acid Media

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Summary: The kinetics of the reaction between iodine and hydrazine was studied spectrophotometrically for full understanding of the proper conditions under which the reaction is fast and quantitative. The hydrogen ions were found to exert an enormous influence to and by the system that results in positive errors of the reaction orders. The reaction was found to be complete within twenty seconds just above pH 4.5. A suitable buffer is recommended to be used for governing the pH decrease during the titration. Hydrazine free base acts as the active reductant and iodine as a two electron oxidant. Nitrogen gas (N_2) was detected by mass spectrometry as the major product for hydrazine oxidation. A possible mechanism for the reaction under certain conditions was suggested.

Keywords: Hydrazine; iodine; hydrogen ions; spectrophotometry and kinetics.

Introduction

Since the year 1890, iodine has been used in Analytical Chemistry for determining the strength of hydrazine solutions. Curtius and Schulz [1] have shown that in alcoholic medium, hydrazine hydrate was quantitatively oxidized by iodine to nitrogen (N_2) gas only. Berthoud and Porrets [3] have studied the reaction kinetically by measuring the rate through estimating the remaining contents of iodine titrimetrically with thiosulphate method. They have shown that the form in which the reaction proceeds is uncertain. The titration method [2] has not been validated yet, since the proper conditions for the quantitative determination and the true mechanism have not been mentioned in the literature. The numerous mechanistic studies on hydrazine oxidation show complications on the system. One and two electron transfer reactions, with particular

reference to hydrazine and common features of the reaction of a large number of oxidizing agents with hydrazine were pointed out [4-12].

Experimental

Reagents

Water

Quartz - processed high purity water was used throughout. The water was deaerated by purging with argon before use.

Iodine

The required amount was dissolved in 20% iodate-free potassium iodide solution containing the appropriate amount of stock acid, stirred at intervals to hasten solution of iodine, and

when all has dissolved diluted to one litre with water. The solution was kept in a flask polished with blacking to protect from light. The iodine solution was then standardized with a standard ascorbic acid solution, a method described by Erdey and Svehla [13].

Hydrazine

Analar hydrazine sulphate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$) was dried at 50°C in a vacuum oven and kept over magnesium perchlorate. The required amount was weighed by difference and dissolved in water containing the appropriate stock acid solution and made to volume.

Sulphuric acid

A stock solution of known concentration was prepared from Analar 98% sulphuric acid. This was accurately standardized against a standard sodium carbonate solution to methyl orange end-point of a colour matched with a blank of corresponding concentration of sodium sulphate to which 0.01 ml of sulphuric acid had been added.

Apparatus

Spectrometers

Beckman model 35 and 5700 spectrophotometers with matched sets of W 210/UU/10.00 mm syndicate cells were used for the ultra-violet region. A Beckman Acculab T.M.4 infra red spectrophotometer with 100 mm gas cell with sodium chloride windows was used. Balzer 311 Quadropole mass spectrometer was also used.

pH meter

Metrohm 632 digital pH meter was used.

Results and Discussion

Absorption spectrum

Absorption of 1×10^{-3} M solution of iodine in 4% potassium iodide was recorded in the wave length range of 200-550 nm. Three absorption maxima were identified at wave length 222, 288 and 350 nm for the iodide (I^-), triiodide (I_3^-) and iodine (I_2) respectively. The absorption maximum for the triiodide at 288 nm was chosen as the working wavelength throughout this work. The evidence for the wavelength assignments is the experimental height of absorbance maxima when taking equilibria into account.

Stoichiometry

Solutions of iodine in excess to hydrazine in the pH range of 0 - 6 were left to react to completion for two hours. The excess of iodine was back titrated with a standard ascorbic acid solution [13]. The stoichiometry of the reaction of iodine to hydrazine was found to be 2:1

Typical reaction curve

Different equimolar solutions of reactants were mixed together at pH varying between 1.0 to 5.0 and absorbance readings were recorded at time intervals. The reaction rate slows down as the acid concentration increases and stops at pH zero. The reaction goes fast at higher pH values of life time 20 second just above pH 4.5 at which the determination is quantitative. Below this value the reaction is not quantitative due to incompleteness of the reaction within the titration run. Moreover, it was also observed that there is a continuous decrease in the pH value after reactants were mixed and remains constant when products are completely

formed. The rate of pH decrease is greater at higher reactants concentrations especially at low acid concentration. However, no linear relation what-so-ever was observed. This phenomenon was clearly manifested by the use of a digital pH meter. The limited solubility of iodine led to consider the triiodide concentration as the one followed spectrophotometrically to investigate for the kinetics of the reaction. All experiments were conducted at 25°C unless otherwise specified.

The order of the reaction with respect to iodine was determined by the integral method [14-17] varying the initial concentration of iodine and keeping the hydrazine and acid constant at higher concentrations, at least hundred times the iodine. Different experiments were conducted at different reactants concentration. The hydrazine was taken in the range 1.0×10^{-2} to 1.0×10^{-3} M whereas sulphuric acid in the range 1.0 to 1.0×10^{-1} M. For each run a first order plot of log of absorbance versus time was plotted by a computer using a least square computer programme, and a typical curve was represented in Fig.(1). A fairly good straight line was obtained with a slope of a constant value of $1.45 \times 10^{-3} \text{S}^{-1}$ being a pseudo first order rate constant (k) of a standard deviation of 5.46×10^{-6} .

The reaction order with respect to hydrazine was determined by the isolation method [4-17] of \log_{10} rates versus log concentration. In the isolation method all reagents except one, the one under study, are arranged in such great excess that their concentrations do not change significantly. Rates of reactions were priorly determined by the variable time method of measurement [14-17] as $\frac{\Delta A}{\Delta t}$; where

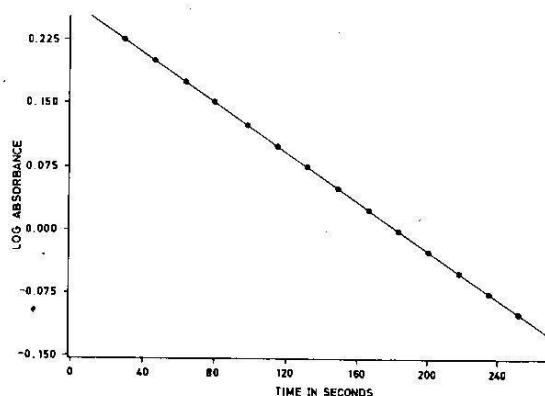


Fig.1: A typical reaction curve for \log_{10} absorbance of $[I_3^-]$ versus time when $[I_2] = 1.2230 \times 10^{-4}$ M

initial concentrations of : $[N_2H_4] = 1.2600 \times 10^{-2}$ M

PH = 0.66

A is absorbance and t is time in seconds. A typical example is shown in Fig (2). Different initial concentrations of hydrazine were taken keeping hydrogen ions and iodine constant for each experiment. Different experiments were conducted in the pH range between 2.20 to 2.85 while iodine concentration ranging between 1.0×10^{-1} to 1.0×10^{-2} M. The reaction order in hydrazine was found to be a first order in the range of pH between 2.2 to 3.0. It was noticed that as the pH, iodine and hydrazine concentration increase, the order also increases as represented in Table (1).

The reaction order with respect to hydrogen ions was also determined by the isolation method and rates by the variable time method as above. Different experiments were conducted, keeping iodine and hydrazine at constant concentrations while varying the hydrogen ions in each experiment. The order was found to be a negative value

Table 1: Reaction order in hydrazine

pH	$[\text{N}_2\text{H}_4]/\text{M}$	$[\text{I}_2]\text{M}$	order
2.20	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.00
2.45	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.00
2.61	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.00
2.84	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.00
3.00	$1.004 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.00
3.28	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.15
3.52	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.33
3.85	$1.0114 - 2.2004 \times 10^{-5}$	1.2576×10^{-2}	1.41
3.28	$1.0114 - 2.2004 \times 10^{-5}$	2.5142×10^{-2}	1.21
3.28	$1.0114 - 2.2004 \times 10^{-5}$	5.0304×10^{-2}	1.29
3.28	$1.0114 - 2.2004 \times 10^{-5}$	7.5456×10^{-2}	1.31
3.28	$1.5013 - 2.8021 \times 10^{-5}$	7.5456×10^{-2}	1.28
3.28	$2.0814 - 3.1815 \times 10^{-5}$	7.5456×10^{-2}	1.33
3.28	$4.1124 - 5.1121 \times 10^{-5}$	7.5456×10^{-2}	1.44

ranging between (zero) to (-1.11) depending upon the acid and reactants concentrations. The order decreases as the reactants concentrations decrease as shown in Table (2). This sequential decrease implies that the order might reach (-2) if the acid concentration is further reduced in a range where rate is too fast to follow.

Arrhenius activation energy was determined by plotting \log_{10} of pseudo first order rate constant (k) (determined by a computer programme) versus $\frac{1}{T}$ where T is temperature in Kelvin,

as in Fig.(3) under varying temperature between 20-40°C; and that was found to be equal to 71.80 KJ mol⁻¹.

By mass spectroscopic technique nitrogen (N₂) gas was detected at mass number 28 as the major product of hydrazine oxidation. A careful search by chemical tests and I.R. technique for other products of nitrogen compounds failed to reveal their presence in detectable amounts.

From the results above and the fact that the reaction rate is retarded

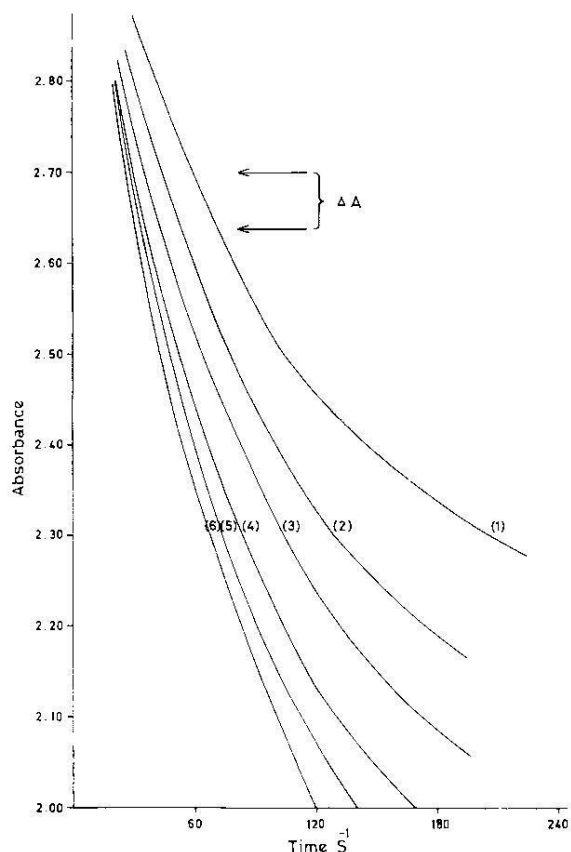


Fig.(2) A typical reaction curve for absorbance versus time at initial PH=3.52

$$[I_2] = 1.2118 \times 10^{-2} M$$

and at the following initial hydrazine concentrations:

- | | |
|-------------------------------|-------------------------------|
| (1) $1.2762 \times 10^{-5} M$ | (4) $2.0410 \times 10^{-5} M$ |
| (2) $1.5313 \times 10^{-5} M$ | (5) $2.2960 \times 10^{-5} M$ |
| (3) $1.7860 \times 10^{-5} M$ | (6) $2.5500 \times 10^{-5} M$ |

by increasing hydrogen ions and accelerated by decreasing the hydrogen ions would lead to the supposition that hydrazine free base ($H_2N.NH_2$) is the active reductant. This could be represented in a fast pre-equilibrium step: $N_2H_5^+ \rightleftharpoons N_2H_4 + H^+$, which is fast at all pH values. This step is

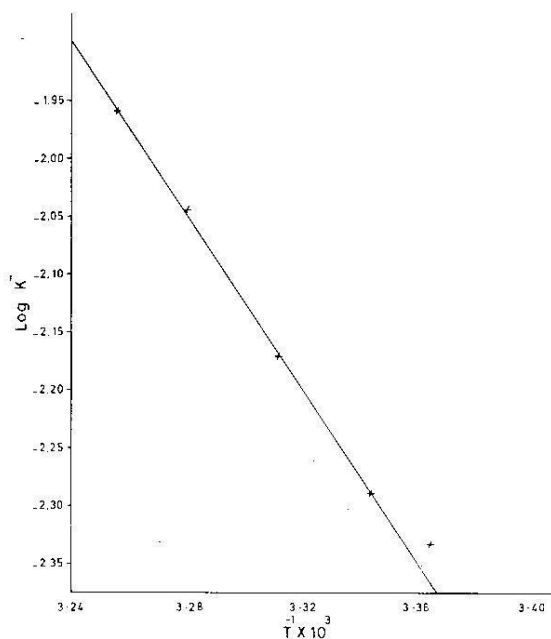


Fig. (3) A typical plot for Arrhenius activation energy of $\log_{10} K$ versus T^{-1}

when $[I_2] = 1.0300 \times 10^{-4} M$

$$[N_2H_4] = 1.1021 \times 10^{-2} M$$

initial PH = 0.37

much faster at higher pH values and the protonated species is expected to proceed irreversibly to the free base at pH greater than 7. On the other hand and at low pH the reactant N_2H_4 converts to the di-protonated $N_2H_6^{2+}$ and the reaction appreciably stops.

The phenomenon that the pH of reactants solution is decreased as the reaction proceeds would simply indicate that hydrogen ions are generated by the system as one of the reaction products. As hydrogen ions are generated, we could certainly expect a decrease in the reaction rate appreciably. Since there is always a decrease in the reaction rate caused by the system itself; a positive error accom-

Table (2) Reaction order in hydrogen ions.

pH range	[I ₂]/M	[N ₂ H ₄]/M	order
0.00 - 1.18	6.6150x10 ⁻⁴	6.0726x10 ⁻⁴	zero
1.22 - 2.00	5.5125x10 ⁻⁴	5.0605x10 ⁻⁴	-0.15
2.00 - 2.50	4.4100x10 ⁻⁴	4.0484x10 ⁻⁴	-0.22
2.20 - 2.84	3.3075x10 ⁻⁴	3.0363x10 ⁻⁴	-0.67
2.41 - 3.00	2.2050x10 ⁻⁴	2.0242x10 ⁻⁴	-0.89
2.50 - 3.12	1.6538x10 ⁻⁴	1.5182x10 ⁻⁴	-1.00
2.62 - 3.20	1.6538x10 ⁻⁴	1.5182x10 ⁻⁴	-1.11

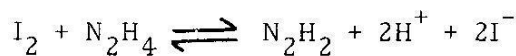
panies the orders of the reaction indefinitely. This effect has been demonstrated by the positive errors in the reaction order in both hydrazine and acid concentrations. On the other hand, the reaction order in iodine has not been affected at all and was always first order. This is likely due to the fact that the iodine concentration in this case was made at most 1/100 times acid and hydrazine concentrations; and that the hydrogen ions produced as the result of the reaction is so low that does not show any change in the pH of the solution. In other words iodine is the only one varied while the hydrazine and the hydrogen ions are constant at higher concentrations.

A rate equation of the following form will be probable for the actual reaction regardless of the influence of hydrogen ions produced by the system.

$$\text{Rate} = \frac{K \cdot [N_2H_4][I_2]}{[H^+]^2}$$

Together with this rate law and the stoichiometry of the reaction, a

two-stage mechanism is likely to take place. Thus hydrazine free base reacts with one molecule of iodine in a slow rate determining step releasing an intermediate of N₂H₂ and H⁺ in the first stage process. This intermediate has already been established by other investigators [4-7]. In the second stage another molecule of iodine reacts with this intermediate giving N₂ gas and H⁺ as the final products. Higginson *et al.* [4] have shown that in a two-stage mechanism in hydrazine reactions by two electron oxidants, the rate is expected to be determined by the first stage only, since the second stage is virtually an independent reaction. A similar mechanism was suggested for hydrazine oxidation by thallium (III) as a two electron oxidant [4,8]. The steps could be summarized as follows:



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