

KINETICS AND MECHANISM OF OXIDATION OF HYDRAZINE BY IODINE IN PRESENCE OF IODIDE IN AQUEOUS ACID MEDIUM

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Abstract: The kinetics of oxidation of hydrazine by iodine in presence of excess iodide has been studied. The reaction is second order and hydrogen ion concentration reduces the rate. The reaction stoichiometry corresponds to the reaction as represented by eqn (1) $2 I_2 + N_2H_4 \rightarrow 4 I^- + N_2 + 4H^+$ (1)

The Kinetic rate law (2) accounts for the proposed mechanism. Thermodynamic parameters have also been

evaluated.
$$-\frac{1}{2} \frac{d[I_2]}{dt} = \frac{k K_2 [N_2H_5^+][I_2]}{K_1 (K_2 + [H^+]) [I^-]}$$
 (2)

Keywords: Kinetics, Hydrazine, Mechanism, Iodine, Oxidation.

INTRODUCTION

A variety of applications of hydrazine as a reducing agent are reported in explosives and rocket propellants apart from synthetic applications in pharmaceutical chemistry[1]. Higginson *et al.*[2] gave a general mechanism of oxidation of hydrazine long back taking into account the classification of one and two electrons oxidation of hydrazine as reported by Kirk and Browne[3]. The oxidation of hydrazine in aqueous solution has been reviewed by Stanbury [4].

The titrimetric analysis of iodine by hydrazine or vice-versa has been employed in analytical chemistry[5]. A large number of studies regarding kinetics and mechanism of oxidation of hydrazine by iodine under varied experimental [6-11] conditions have been reported as reviewed by Margerum *et al.*[12] in recent publication and there are number of contradictions in these studies

both of kinetics and mechanisms. Since the detailed study of this reaction has been reported by employing pulsed accelerated flow spectrometer[13], still certain queries are to be replied. In view of these observations we have undertaken the title study from the following view-point. First the kinetics of the title reaction has been carried out in appreciably high concentration of iodide. Secondly phosphate buffer catalysis due to formation of $N_2H_4.HPO_4^{3-}$ complex has been reported [12] which appears to be untenable in the light of nucleophilic nature of both these species and thirdly it will be interesting to understand the trend of the reaction in the presence of acetate buffers.

RESULTS

(1) Hydrazine Dependence

The concentration of hydrazine was varied from 1.0×10^{-3} to 5.0×10^{-3} mol dm⁻³ at three different but fixed concentrations of iodine to be 2.0×10^{-3} ,

4.0×10^{-3} and 5.0×10^{-3} mol dm⁻³ respectively also keeping constant concentration of other reaction ingredients *viz.* [KI] = 2.0×10^{-2} mol dm⁻³, [HClO₄] = 0.1 mol dm⁻³ at 35°C. Initial rates were calculated¹⁴ and a plot of initial rate (k_i , mol dm⁻³ sec⁻¹) versus hydrazine concentration yielded a straight line passing through the origin confirming first order dependence with respect to the latter.

(2) Iodine Dependence

The concentrations of iodine was varied in the range $(1.0-5.0) \times 10^{-3}$ mol dm⁻³ at two fixed concentrations of hydrazine to be 2.0×10^{-3} and 5.0×10^{-3} mol dm⁻³ at fixed concentrations of other reaction ingredients *viz.* [KI] = 2.0×10^{-2} mol dm⁻³, [HClO₄] = 0.1 mol dm⁻³ at 35°C. Initial rates were evaluated and a plot of initial rate versus concentration of iodine yielded a straight line passing through the origin indicating first order with respect to iodine. Second order plots were also made and the second order rate constants evaluated from these plots are in agreement with the rate constants calculated from initial rates.

(3) Hydrogen Ion Dependence

The concentration of hydrogen ion was varied by employing perchloric acid at fixed concentrations of other reaction ingredients *viz.* [N₂H₅⁺] = 2.0×10^{-3} mol dm⁻³, [I₂] = 2.0×10^{-3} mol dm⁻³, [KI] = 2.0×10^{-2} mol dm⁻³ at temperatures 35°, 40° and 45°C respectively. The rate of the reaction decreases with increasing hydrogen ion concentration and then tends to attain a limiting rate at higher hydrogen ion concentrations.

(4) Variation of Potassium Iodide

The concentration of potassium iodide was varied from 2.0×10^{-2} to 5.0×10^{-1} mol dm⁻³ at fixed concentrations of other reaction ingredients *viz.* [N₂H₅⁺] = 2.0×10^{-3} mol dm⁻³, [I₂] = 2.0×10^{-3} mol dm⁻³, [HClO₄] = 0.1 mol dm⁻³ at I = 1.0 mol dm⁻³ and 30°, 35° and 40°C respectively. The rate decreases with increasing concentration of iodide.

(5) Test of Free-Radicals

The test of free radicals was also made by adding acrylic acid in the reaction mixture. However, monomer does not polymerize even after sufficient lapse of time as no white precipitate was observed.

(6) Temperature Dependence

The reaction has also been studied at three temperatures *viz.* 35°, 40° and 45°C respectively keeping fixed concentrations of other reaction ingredients constant. A plot of log k (dm³ mol⁻¹ sec⁻¹) was made against 1/T that yielded a straight line. The energy of activation was calculated from the slope to be 72 ± 6 kJ mol⁻¹. The entropy of activation was calculated in a conventional manner employing eqn (3.2)

$$k = \frac{k_b T}{h} \cdot e^{-E_a^\ddagger / RT} \cdot e^{\Delta S^\ddagger / R} \dots\dots\dots(1)$$

to be $(-)(45 \pm 5)$ JK⁻¹ mol⁻¹.

STOICHIOMETRY

The stoichiometry of the reaction was determined by allowing reactions with excess of iodine over hydrazine in a thermostated water-bath at $\pm 01^\circ\text{C}$ for Ca. 4h. The excess of iodine was estimated by titrating against thiosulphate using starch as indicator. The results as collected in Table 1

support the reaction as represented by eqn (2)



Similar stoichiometry has also earlier been reported.[13]

Table 1

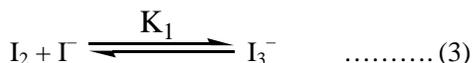
pH = 1, 35°C

$[N_2H_5^+]$ mol dm ⁻³	$[I_2]$ mol dm ⁻³	$D[I_2] / D[N_2H_5^+]$
0.002	0.006	2:1
0.002	0.008	2:1
0.002	0.01	2:1
0.004	0.01	2:1

$D[I_2]$ and $D[N_2H_5^+]$ represent consumed iodine and hydrazine respectively.

DISCUSSION

Since the reaction has been studied in the presence of excess iodide ion concentration, the equilibrium (3) is immediately established converting iodine to iodonium ion.



K_1 is reported¹⁵ to be $5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$.

Further rate of the reaction is retarded by hydrogen ion concentration, such an effect of hydrogen ion can not be co-related to either iodine or iodonium ion.

Hydrazine exists in the protonated form in acid solutions since the acid dissociation constant for protonated hydrazine is reported¹⁶ to be $1.2 \times 10^{-1} \text{ mol dm}^{-3}$ at 25°C.



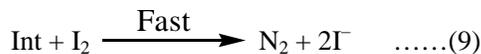
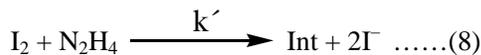
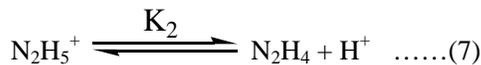
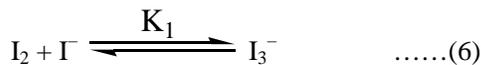
The $N_2H_6^{2+}$ species of hydrazine is also reported but no conclusive evidence has yet been adduced.



Since rate decreases with increasing hydrogen ion concentration, N_2H_4 appears to be the reactive form of hydrazine. However, $N_2H_5^+$ has also been considered to be the reactive species of hydrazine in other reactions[17,18].

The complexation has been reported[18,19,20] between certain metal ions and hydrazine whereas there are also reactions reported[21,22,23] to occur without any complex formation such complexation between iodine and hydrazine has been observed neither kinetically nor spectrally. Moreover, order with respect to each reactant is one. Rate decreases with increasing hydrogen ion concentration.

Considering all these experimental observations and also iodine and N_2H_4 to be the reactive species of iodine and hydrazine respectively, following reaction mechanism can be envisaged



Such a mechanism and loss of iodine lead to the rate law (10) or (11)

$$-\frac{d[I_2]}{dt} = \frac{2k'K_2[N_2H_5^+][I_2]}{K_1(K_2 + [H^+])[I^-]} \quad \dots\dots\dots(10)$$

Where $[N_2H_5^+]$ and $[I_2]$ are gross analytical concentrations of hydrazine and iodine respectively.

or

$$-\frac{d[I_2]/dt}{[N_2H_5^+][I_2]} = k = \frac{2k'K_2}{K_1(K_2 + [H^+])[I^-]} \quad \dots\dots\dots(11)$$

Since $[H^+] \gg K_2$, rate law (11) reduces to (12)

$$k = \frac{2k'K_2}{K_1[I^-][H^+]} \quad \dots\dots\dots(12)$$

or

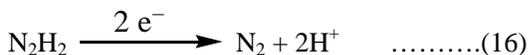
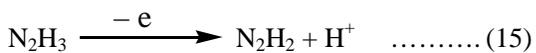
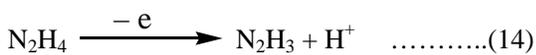
$$k = k''[\Gamma][H^+]^{-1} \quad \dots\dots (13)$$

where $k'' = 2k'K_2/K_1$

A plot of $(k[\Gamma])$ versus $[H^+]^{-1}$ was made from eqn (12) that yielded a straight line passing through the origin. Moreover, 'k' versus $[\Gamma]^{-1}$ plot was also made at constant hydrogen ion concentration that also yielded a straight line passing through origin .

k'' was calculated from the slope of the line of plot. k' can be evaluated provided ' K_2 ' and ' K_1 ' are known under experimental conditions.

Now the question is regarding the intermediate in the reaction mechanism and its pattern of reaction. It has earlier been reported[24, 25] that during one electron oxidation of hydrazine by any oxidant, hydrazyl radical is formed which on dimerization subsequently decomposes to nitrogen and ammonia. Since iodine is a two electron compound and in the formation of nitrogen from hydrazine four electrons change is required, hydrazyl intermediate in one electron change is formed[26, 27].

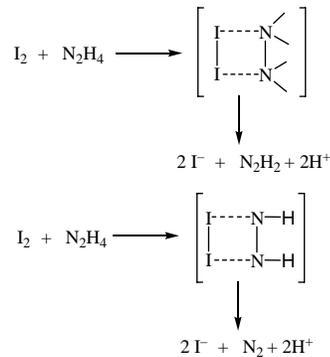


The oxidation of hydrazine by different oxidants reportedly takes place in two paths depending on whether the oxidant is a one or two electron reagent[15, 28]. In the light of these observations the intermediate must be hydrazine species.

Since no free radical test has been found positive, it is reasonable to assume that such species as intermediate after formation remains in the solvent

cage and rapidly reacts in it before diffusing out. This negates formation of free radical in the reaction and in turn negates free radical test.

Such an intermediate can also be suggested.



A though negative entropy of activation supports such an more ordered transition state, no evidence otherwise supports such a proposition. However, ultimate fate of such a proposal is the same as reported earlier.

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