

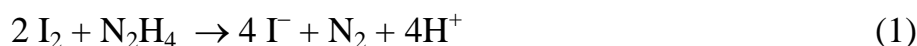
Effect of Hydrogen on Kinetics of Oxidation of Hydrazine with Solution Acid

Dr Madhu Shrimal, HOD , Arya college of Engineering &it

Email: madhushrimal@gmail.com

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)



The Kinetic rate law (2) accounts for the proposed mechanism.

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

Keywords: kinetics, Mechanism, Oxidation, Hydrazine, Iodine

Indroduction:

Hydrazine was acted as reducing agent.

Higginson *et al.*¹ 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.² 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 spectrometer⁴, 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 reaction has been taken out in appreciably high concentration of iodide.

Secondly phosphate buffer catalysis due to formation of $N_2H_4.HPO_4^{3-}$ complex has been reported³ which appears to be untenable in the light of nucleophilic nature of both these species

and thirdly the reaction is to be understand in the presence of acetate buffers.

EXPERIMENTAL

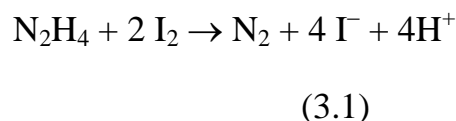
All the chemicals employed in this study were either of E. Merck or G.R. quality.

KINETIC PROCEDURE

The kinetics were monitored by withdrawing an aliquot (5 or 10 cm³) at different time intervals and then quenched in an ice-cold dil. H₂SO₄ (~ 1.0 mol dm⁻³), the remaining iodine was assayed by titrating against thiosulphate solution using starch as an indicator.

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.



Similar stoichiometry has also earlier been reported.³ Thus the stoichiometry of reaction with respect to $\Delta[I_2] / \Delta[N_2H_5]$ is 2:1.

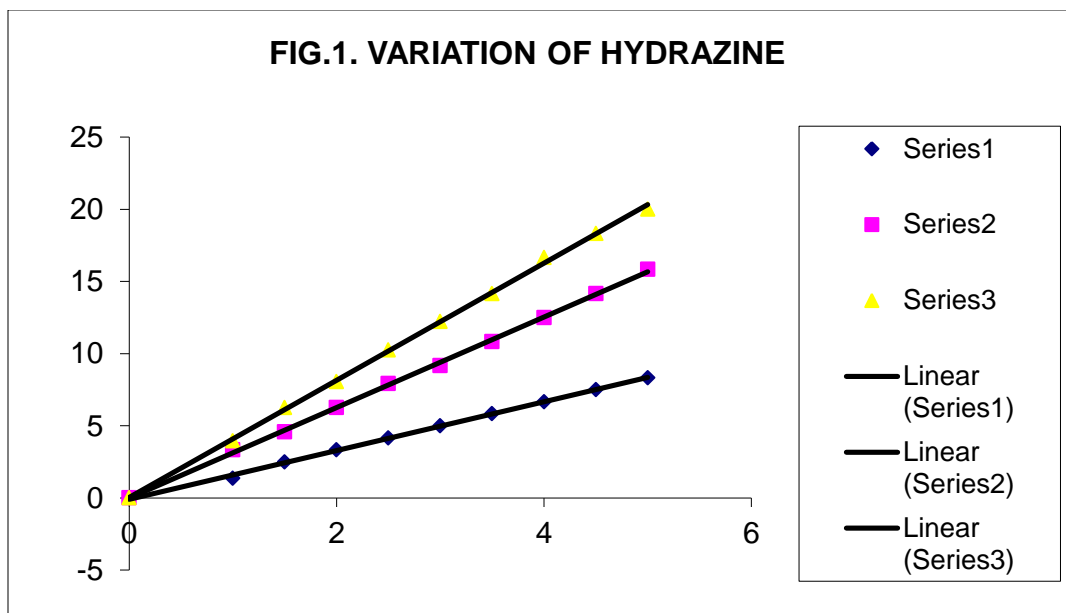
RESULT

(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. A

plot of initial rate (k_i , mol dm^{-3} sec^{-1}) versus hydrazine concentration yielded a straight line passing through the origin (Fig. 1) confirming first order dependence with respect to the latter.

Since these concentrations of the reactants are comparable, second order plots were also constructed and the second order rate constants were evaluated .



(2) Iodine Dependence

The concentrations of iodine was varied in the range $(1.0-5.0) \times 10^{-3} \text{ mol dm}^{-3}$ at two fixed concentrations of hydrazine to be 2.0×10^{-3} and $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ at fixed concentrations of other reactants. 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 (Fig. 2). 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. Results are given in Table 1,2.

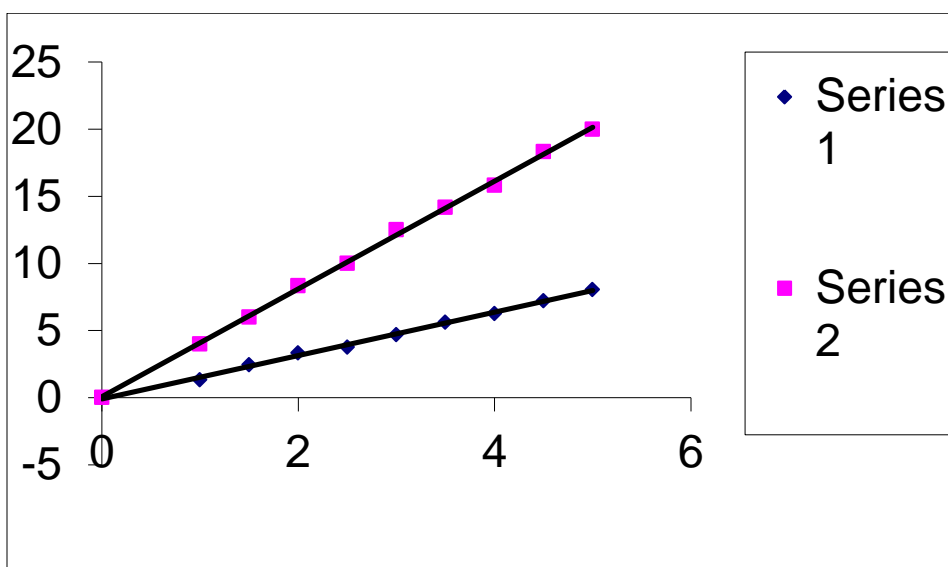


Fig 2 A Plot Of $[I_2]$ Versus K_i

Table-1

VARIATION OF IODINE SOLUTION

$[N_2H_5] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temp. = 35°C

$[HClO_4] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$

Titrant [Hypo] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

$[KI] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$

Aliquot = 5.0 ml

$10^3 [I_2], \text{ mol dm}^{-3}$	1.0	1.5*	2.0*	2.5**	3.0**	3.5***	4.0** *	4.5*** *	5.0*** *
Time in minutes	Volume of Hypo used in ml								
0	4.2	3.7	4.8	3.7	4.8	4.2	4.8	4.6	4.7
1	3.7	3.0(1)	3.7(1)	3.2(2)	3.8(2)	3.5(1)	4.2(1)	4.3(1)	4.0(1)
2	3.4	2.7(3)	2.8(3)	3.0(4)	3.3(4)	3.4(2)	4.0(2)	4.0(3)	3.6(3)
3	3.2	2.5(6)	2.3(6)	2.6(6)	3.0(6)	3.0(3)	3.8(3)	3.5(6)	3.0(6)
4	2.9	2.1(9)	1.9(9)	2.2(8)	2.6(8)	2.7(4)	3.6(4)	3.0(9)	2.7(9)
6	2.5	1.8(12)	1.6(12)	1.9(10)	2.3(10)	2.5(6)	3.1(6)	2.7(12)	2.4(12)
8	2.1	1.4(15)	1.3(15)	1.7(12)	2.0(12)	2.2(8)	2.9(8)	2.2(15)	2.0(15)
10	1.7	1.0(18)	1.1(18)	1.5(14)	1.6(16)	2.0(10)	2.7(10)	1.8(18)	1.8(18)
12	1.5	0.7(21)	0.9(21)	1.2(16)	1.4(20)	1.7(12)	2.4(12)	1.5(24)	1.4(24)
14	1.3	-	-	1.2(20)	-	1.4(16)	2.2(16)	-	1.2(30)
$10^6 (ki), \text{ mol dm}^{-3} \text{ sec}^{-1}$	1.66	2.44	3.33	3.75	4.68	5.625	6.25	7.22	8.05
$(k), \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$	0.83	0.84	0.77	0.77	0.77	0.77	0.77	0.81	0.77

*Titrant [Hypo] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$

** Titrant [Hypo] = 6.0×10^{-3} mol dm⁻³

*** Titrant [Hypo] = 8.0×10^{-3} mol dm⁻³

**** Titrant [Hypo] = 10.0×10^{-3} mol dm⁻³

Figures in parentheses denote time in minutes.

Table-2
VARIATION OF IODINE SOLUTION

[N₂H₅] = 5.0×10^{-3} mol dm⁻³

Temp. = 35°C

[HClO₄] = 1.0×10^{-1} mol dm⁻³

Titrant [Hypo] = 2.0×10^{-3} mol dm⁻³

[KI] = 2.0×10^{-2} mol dm⁻³

Aliquot = 5.0 ml

10 ³ [I ₂], mol dm ⁻³	1.0	1.5*	2.0*	2.5**	3.0**	3.5***	4.0***	4.5****	5.0****
Time in minutes	Volume of Hypo used in ml								
0	4.5	5.0	5.0	3.7	5.0	4.3	4.5	4.5	4.7
1	3.8	3.3(0.5)	3.8(1)	3.0(1)	3.7(1)	3.8(1)	3.3(1)	3.4(1)	3.2(1)
2	3.2	3.0(1)	3.3(2)	2.5(2)	3.3(2)	3.0(2)	2.8(2)	2.8(2)	2.7(2)
3	2.6	2.5(2)	2.8(3)	2.2(3)	3.0(3)	2.5(3)	2.5(3)	2.4(3)	2.2(3)
4	2.1	2.3(3)	2.3(4)	2.0(4)	2.6(4)	2.2(4)	2.0(4)	2.1(4)	2.0(4)
5	1.7	2.0(4)	2.0(5)	1.7(5)	2.0(6)	1.4(6)	1.8(5)	1.8(5)	1.7(5)
6	1.5	1.8(5)	1.8(6)	1.6(6)	1.6(8)	1.0(8)	1.5(6)	1.5(6)	1.5(6)
7	1.3	1.7(6)	1.3(8)	1.5(7)	1.4(10)	0.8(10)	1.2(8)	1.2(8)	1.3(8)
8	1.1	-	-	-	-	0.8(12)	-	0.8(10)	-
10 ⁶ (ki), mol dm ⁻³ sec ⁻¹	4.0	6.0	8.33	10.0	12.5	14.166	15.83	18.33	20.0
(k), mol ⁻¹ dm ³ sec ⁻¹	0.81	0.81	0.815	0.82	0.83	0.83	.077	0.83	0.84

*Titrant [Hypo] = 4.0×10^{-3} mol dm⁻³

** Titrant [Hypo] = 6.0×10^{-3} mol dm⁻³

*** Titrant [Hypo] = 8.0×10^{-3} mol dm⁻³

**** Titrant [Hypo] = 10.0×10^{-3} mol dm⁻³

Figures in parentheses denote time in minutes.

(3) Hydrogen Ion Dependence

The concentration of hydrogen ion was varied by employing perchloric acid at fixed concentrations of other reaction ingredients viz. $[N_2H_5^+] = 2.0 \times 10^{-3} \text{ dm}^{-3}$, $[I_2] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[KI] = 2.0 \times 10^{-2} \text{ mol}$

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 (Fig. 4). Results are given in Tables 3,4,5.

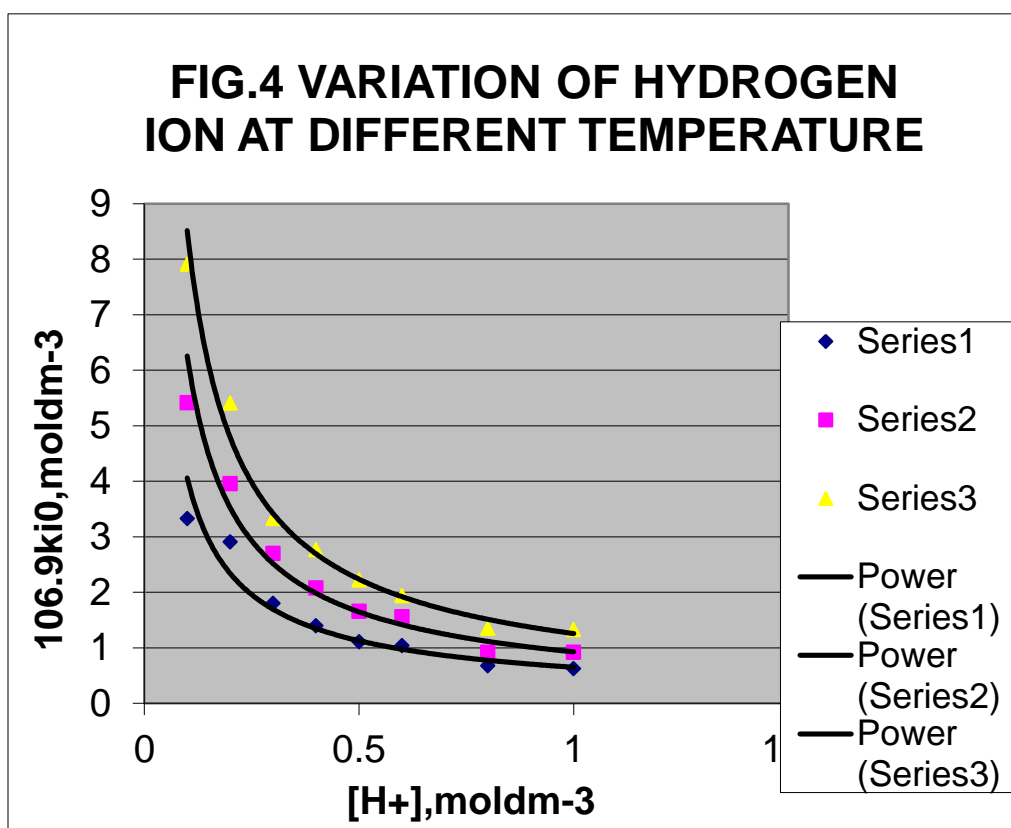


Table-3

VARIATION OF HYDROGEN ION

$[N_2H_5] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temp. = 35°C

$[I_2] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$

Titrant [Hypo] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$

$[KI] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$

Aliquot = 5.0 ml

[HClO ₄], mol dm ⁻³	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
Time in minutes	Volume of Hypo used in ml							
0	4.8	5.0	5.0	5.0	5.0	5.0	5.0	5.0
1	3.7	4.5	4.2(3)	4.3(3)	4.4(3)	4.5(3)	4.6(4)	4.7(4)
3	2.8	4.2	3.8(6)	4.0(6)	4.1(6)	4.2(6)	4.2(8)	4.5(8)
6	2.3	3.7	3.5(9)	3.4(12)	3.6(12)	4.0(12)	4.0(12)	4.2(12)
9	2.0	3.2	3.1(12)	3.0(18)	3.2(18)	3.5(18)	3.8(16)	3.9(16)
12	1.6	2.8	2.5(18)	2.6(24)	3.0(24)	3.1(24)	3.5(24)	3.6(24)
15	1.3	2.4	2.2(24)	2.2(30)	2.5(30)	2.9(30)	3.0(32)	3.4(32)
18	1.1	2.1	1.7(30)	1.9(36)	2.2(36)	2.6(36)	2.7(40)	3.1(40)
21	0.9	1.8(24)	-	-	-	2.0(42)	2.2(48)	2.6(48)
10 ⁶ (ki), mol dm ⁻³ sec ⁻¹	3.33	2.91	1.8	1.4	1.11	1.04	0.677	0.625

Figures in parentheses denote time in minutes.

Table-4

VARIATION OF HYDROGEN ION

$$[\text{N}_2\text{H}_5] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Temp.} = 40^\circ\text{C}$$

$$[\text{I}_2] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Titrant } [\text{Hypo}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{KI}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Aliquot} = 5.0 \text{ ml}$$

[HClO ₄], mol dm ⁻³	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
Time in minutes	Volume of Hypo used in ml							
0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
1	4.2	4.0(2)	4.2(2)	4.3(2)	4.4(2)	4.5(2)	4.6(2)	4.5(4)
2	3.8	3.5(4)	3.8(4)	4.0(4)	4.1(4)	4.2(4)	4.2(4)	4.2(8)
3	3.4	3.0(6)	3.5(6)	3.4(8)	3.6(8)	4.0(8)	4.0(8)	3.9(12)
4	3.1	2.6(8)	3.1(8)	3.0(12)	3.2(12)	3.5(12)	3.8(12)	3.6(18)
6	2.6	2.3(10)	2.5(12)	2.6(16)	3.0(16)	3.1(16)	3.5(18)	3.4(24)
8	2.2	2.0(12)	2.2(16)	2.2(20)	2.5(20)	2.9(20)	3.0(24)	3.1(30)
10	1.8	1.8(14)	1.7(20)	1.9(24)	2.2(24)	2.6(24)	2.7(30)	2.6(36)
12	1.4	1.4(20)	-	-	-	2.0(28)	2.2(36)	2.4(42)
10 ⁶ (ki), mol dm ⁻³ sec ⁻¹	5.416	3.96	2.7	2.08	1.66	1.56	0.92	0.92

Figures in parentheses denote time in minutes

Table-5

VARIATION OF HYDROGEN ION

$$[\text{N}_2\text{H}_5] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Temp.} = 45^\circ\text{C}$$

$$[\text{I}_2] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Titrant [Hypo]} = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{KI}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Aliquot} = 5.0 \text{ ml}$$

[HClO ₄], mol dm ⁻³	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
Time in minutes	Volume of Hypo used in ml							
0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
1	3.9	4.3(1)	4.0(2)	4.3(1)	4.4(1)	4.5(1)	4.3(2)	4.5(1)
2	3.4	4.0(2)	3.6(4)	4.0(3)	4.0(3)	4.1(3)	4.1(4)	4.3(5)
3	2.9	3.3(4)	3.1(6)	3.4(6)	3.6(6)	3.8(6)	3.8(8)	3.8(10)
4	2.5	2.9(6)	2.7(8)	3.0(9)	3.2(9)	3.4(9)	3.4(12)	3.4(15)
5	2.3	2.4(8)	2.4(10)	2.7(12)	2.9(12)	3.1(12)	2.9(16)	3.0(20)
6	2.0	2.0(10)	2.1(12)	2.2(15)	2.4(15)	2.7(15)	2.4(20)	2.6(25)
8	1.6	1.7(12)	1.7(16)	1.8(18)	2.0(18)	2.4(18)	2.1(24)	2.2(30)
10	1.2	1.3(16)		1.5(21)	1.8(21)	2.1(21)	1.9(28)	1.7(35)
10 ⁶ (ki), mol dm ⁻³ sec ⁻¹	7.91	5.41	3.33	2.77	2.22	1.94	1.35	1.33

Figures in parentheses denote time in minute

(4) 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. The energy of activation was calculated to be 72±6 kJ mol⁻¹. The entropy of activation was calculated in a conventional manner employing eqn (2)

$$k = \frac{k_b T}{h} \cdot e^{-E_a^\ddagger / RT} \cdot e^{\Delta S^\ddagger / R} \quad (2)$$

to be (-) (45±5) JK⁻¹ mol⁻¹.

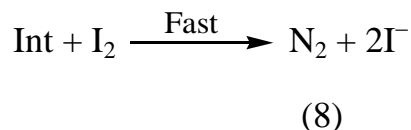
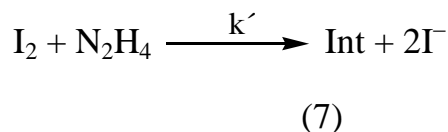
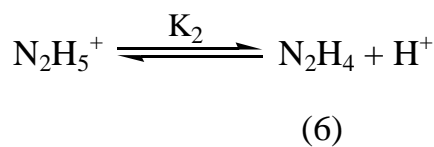
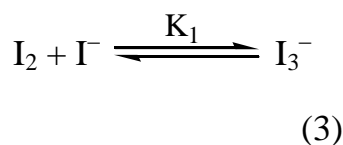
CONCLUSION

Rate of the reaction is decreased by hydrogen ion concentration, such an effect of hydrogen ion can not be correlated to either iodine or iodonium ion.

Since rate decreases with increasing hydrogen ion concentration, N₂H₄

appears to be the reactive form of hydrazine. However, N₂H₅⁺ has also been considered to be the reactive species of hydrazine in other reactions^{5,6}.

Considering all these experimental observations and also iodine and N₂H₄ to be the reactive species of iodine and hydrazine respectively, following reaction mechanism can be envisaged



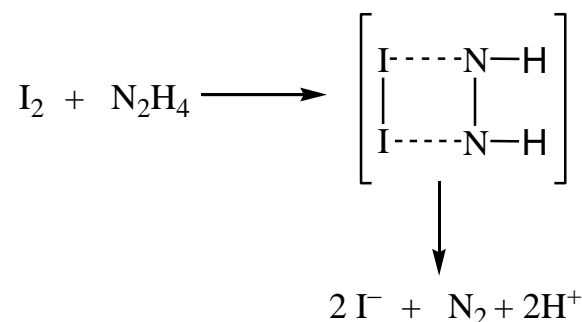
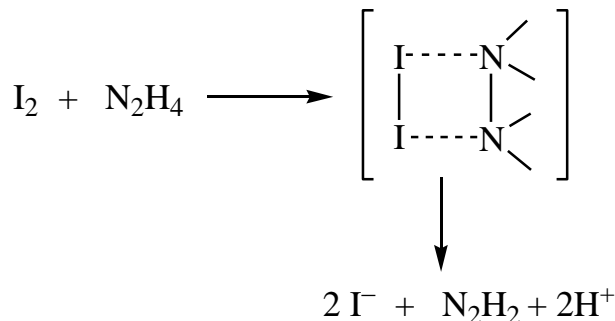
Such a mechanism and loss of iodine lead to the rate law (9) or (10)

$$-\frac{d[I_2]}{dt} = \frac{2k_1K_2[N_2H_5^+][I_2]}{K_1(K_2 + [H^+])[I^-]} \quad (9)$$

It has earlier been reported^{7,8} 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^{9,10}.

Such an intermediate can also be suggested.



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