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CHAPTER - V

PREPARATION
ESTIMATIONS
AND
EXPERIMENTAL

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Preparations, Estimations and Experimental

The hydrazides by known method[1] were prepared in the laboratory. They were prepared by refluxing equimolecular mixtures of methyl ester of corresponding acids and hydrazine hydrate (80 %) in alcohol on the water bath till there is disappearance of layers. The time required for this disappearance of layers is different for different hydrazides. On cooling, white fine needle shaped crystals separates out. Further they are recrystallized and their purity were checked by observing their physical constants i.e. melting points. Two hydrazides prepared were 3-5-dinitrobenzoic acid hydrazide (M.P. 150°C) and p-Methoxy benzoic acid hydrazide (M.P.127°C) .

The standard solutions required for various experiments were prepared as follows:

1) Hydrazides :

To prepare solutions of [0.01 M] hydrazides calculated amount of hydrazides were taken and dissolved in methyl alcohol.

2) Chloramine-T :

Chloramine-T (Fluka A.R.) was used for preparation of solution. To prepare [0.01 M] solution of chloramine-T calculated amount of it was dissolved in required quantity of distilled water.

3) Sodium thio sulphate solution :

2.480 grams of sodium thio sulphate of B.D.H. A.R.grade was dissolved in one litre of distilled water to prepare [0.01 M] stock solution. Before the experiment 100 ml of stock solution was diluted to one litre by distilled water to prepare [0.001 M] solution.

4) Potassium iodide solution : 10 %

5) Sulphuric acid : 2.0 N

6) Buffer Solution :

a) Sodium carbonate (0.025) M solution

2.65 grams of sodium carbonate of BDH A.R.grade was dissolved in one litre of distilled water to prepare (0.025) M sodium carbonate solution.

b) Sodium bicarbonate (0.025) M solution

2.1 grams of sodium bi carbonate of BDH A.R.grade was dissolved in one litre of distilled water to prepare (0.025) M sodium bicarbonate solution.

c) Buffer solution

To prepare 8.88 pH solution 10 ml of 0.025 M sodium bicarbonate and 10 ml of 0.025 M sodium carbonate solutions were mixed in reaction flask. Similarly to prepare 8.55, 9.28 and 9.55 pH solutions 5, 15 and 20 mls of both solutions (sodium bicarbonate and carbonate) are mixed in reaction flasks.

Indicator : Starch solution

Procedure :-

In a 100 ml standard round bottom flask 25 ml of distilled water, 40 ml of methanol, 20 ml of buffer solution and 10 ml of hydrazide solution were mixed and the flask was kept in a thermostate till its contents acquire the temperature of the bath. The addition of 5 ml of chloramine-T solution takes total volume to 100 ml. Thenafter addition of 5 ml of chloramine-T solution, immediately 10 ml aliquote of this reaction mixture was taken and mixed with 5 ml of 10 % potassium iodide and 10 ml of 2.0 N sulphuric acid which were already taken in iodine flask. This mixture is allowed to stand for 10 minutes and the liberated iodine was titrated against (0.001) N sodium thiosulphate solution, using starch as an indicator. This is a initial reading "a". then after definite intervals (10 or 5 minutes) 10 ml of aliquote of the reaction mixture was titrated with using above procedure. From titration readings rate constant (k) was calculated.

a = Initial concentration of chloramine-T in terms of 0.001 N sodium thiosulphate

x = Amount of chloramine-T consumed in time interval (t) in terms of 0.001 N $Na_2S_2O_3$

t = time.

The formula that is used to calculate the rate constant(k) was

$$K = \frac{2.303}{t} \log \frac{a}{(a - x)} \quad \ldots \quad (5.1)$$

Activation Parameters

The above experiments were conducted at different temperatures and rate constants (k) were determined. With the help of data collected, activation parameters were calculated by using following equations :

1) Energy of Activation (Ea)

$$Ea = \log \frac{k_2}{k_1} \left[\frac{T_2 \times T_1}{T_2 - T_1} \right] \times 4.576$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 .

2) Frequency Factor (A)

$$K = A\, e^{-Ea/RT}$$

$$\text{i.e.} \quad \log A = \log K + \frac{Ea}{RT} \log 2.7183$$

3) Entropy of activation (ΔS^*)

$$\log k = \log e + \log \frac{KT}{h} + \left[\frac{\Delta S}{R} - \frac{E}{RT} \right] \log e$$

Introducing the values of all constants

K - Boltzmann constant = $1.3805\ NO^{-16}$

h - Plank's constant = $6.2656\ NO^{-27}$

e - constant = 2.717

R - Gas constant = 1.987

then

$$\Delta S^* = 4.576[\ \log k + 10.576 - \log T + \frac{Ea}{4.576xT}\ ]$$

4) Enthalpy $[\Delta H^*]$

$$\Delta H^* = Ea - RT$$

5) Free Energy $[\Delta G^*]$

$$\Delta G^* = \Delta H - T\Delta S^* .$$

Product Analysis :

Detection of p-Toluene sulphonamide has been done by paper chromatographic method. Benzyl alcohol with water was used as the solvent and 0.5 % vanillin in 1 % hydrochloric acid solution in ethanol was used as the spraying agent. Rf value was found to be 0.905. The oxidation product of hydrazides (R.CONHNHCOR) are identified by isolation and preparation of their derivatives and determination of their physical constants. It is also identified by TLC with the authentic samples prepared by literature method. Nitrogen evolved in the reaction is collected similar to Dumas method[2] is identified.

References

1) Smith, P.A.S.
"Organic Reactions" Vol.III Ed. Rogen Adam, John Wiley and Sons Inc New York, London, Sydney p.367 (1946).

2) Flaschka,H.A. and Barnard A.J.
"Introduction of principles of qualitative analytical chemistry" Barnes & Noble Inc New York Vol I 536 (1969)

TABLE NO. 1

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION

Substrate concentration = [3.5 DNBH] = 0.5×10^{-3}M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88 Temp. = 40° C

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes (t)	(a-x) ml	$k_1 \times 10^2$ min^{-1}
1	0	10.5 (a)	-
2	10	9.0	1.541
3	20	7.7	1.551
4	30	6.5	1.598
5	40	5.7	1.527
6	60	4.5	1.412
7	80	3.4	1.409
		Mean	1.506

TABLE NO. 2

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION

Substrate concentration = [p-MBH] = 3×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88

Temp. = 40° C

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	k x 10^{2} min^{-1}
1	0	10.3 (a)	-
2	10	9.2	1.129
3	20	8.3	1.096
4	40	7.0	0.965
5	60	6.0	0.900
6	80	5.3	0.830
7	100	4.5	0.828
		Mean	0.933

TABLE NO. 3

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF TEMPERATURE ON THE REACTION

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = 50° C pH = 8.88

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	$k_1 \times 10^{-2}$ min^{-1}
1	0	10.2 (a)	-
2	5	7.8	5.310
3	10	6.1	5.306
4	15	4.5	5.205
5	20	3.5	5.360
6	25	2.8	5.174
7	30	2.2	5.105
		Mean	5.294

TABLE NO. 4

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF TEMPERATURE ON THE REACTION

Substrate concentration = [p-MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = 45° C pH = 8.88

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	k x 10^{2} min^{-1}
1	0	10.1 (a)	-
2	10	8.6	1.625
3	20	7.4	1.573
4	30	6.6	1.436
5	40	5.9	1.362
6	60	4.7	1.258
7	80	3.8	1.243
8	100	3.2	1.240
		Mean	1.416

TABLE NO. 5

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE IN REAGENT CONCENTRATION

Substrate concentration = [p-MBH] = 4×10^{-3} M

Chloramine-T concentration = 15×10^{-4} M

pH = 8.88 Temp. 40^{o} C

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	$k \times 10^{-2}$ min^{-1}
1	0	30.0 (a)	-
2	10	26.2	1.354
3	20	23.2	1.200
4	30	21.8	1.095
5	40	19.6	1.064
6	60	16.6	0.987
7	80	14.5	0.908
8	100	12.5	0.900
		Mean	1.107

TABLE NO. 6

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE IN SOLVENT COMPOSITION ON REACTION

Substrate concentration = [3.5DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88 Temp. 40° C

Medium = Methanol/water (70/30 v/v)

Sr. No.	Time in minutes(t)	(a - x) ml	k x 10^{2} min^{-1}
1	0	10.3 (a)	-
2	5	9.1	2.577
3	10	7.9	2.535
4	15	6.9	2.539
5	25	5.6	2.438
6	35	4.6	2.412
7	45	3.7	2.336
8	55	3.3	2.304
		Mean	2.434

TABLE NO. 7

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE IN SOLVENT COMPOSITION ON REACTION

Substrate concentration = [CP-MNBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88 Temp. = 40^{o} C

Medium = Methanol/water (30/70 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	$k \times 10^{2}$ min^{-1}
1	0	10.4 (a)	-
2	10	8.8	1.866
3	20	7.9	1.865
4	40	5.9	1.629
5	60	4.6	1.600
6	80	3.7	1.560
7	100	3.1	1.500
8	120	2.8	1.475
		Mean	1.641

TABLE NO. 8

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE OF pH ON THE REACTION

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = 40° C pH = 9.28

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes (t)	(a-x) ml	$k \times 10^{2}$ min^{-1}
1	0	10.4 (a)	-
2	5	8.9	3.115
3	10	7.6	3.113
4	20	5.7	3.007
5	30	4.2	3.022
6	40	3.2	2.947
7	50	2.4	2.941
8	60	2.0	-
		Mean	3.022

TABLE NO. 9

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF CHANGE OF pH ON THE REACTION

Substrate concentration = [p-MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = $40^{\circ}C$ pH = 8.55

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes (t)	(a-x) ml	$k \times 10^{2}$ min^{-1}
1	0	10.2 (a)	-
2	10	8.9	1.278
3	20	7.8	1.242
4	30	7.2	1.142
5	40	6.6	1.078
6	60	5.8	0.937
7	80	4.8	0.917
		Mean	1.100

TABLE NO. 10

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF THE ADDITION OF SODIUM CHLORIDE ON THE REACTION

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = 40° C pH = 8.88

Salt concentration = [NaCl] = 1×10^{-2} M

Medium = Methanol/water [50/50 v/v]

Sr. No.	Time in minutes(t)	(a-x) ml	$k \times 10^{2}$ min^{-1}
1	0	10.5 (a)	-
2	5	9.0	3.083
3	10	7.8	2.945
4	15	6.7	2.995
5	20	5.8	2.968
6	30	4.5	2.726
7	40	3.5	2.747
8	50	2.8	2.743
		Mean	2.889

TABLE NO. 11

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF THE ADDITION OF SODIUM CHLORIDE ON THE REACTION

Substrate concentration = [p-MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temp. = $40^{\circ}C$ pH = 8.88

Salt concentration = [NaCl] = 1×10^{-2} M

Medium = Methanol/water (50/50 v/v)

Sr. No.	Time in minutes(t)	(a-x) ml	$k \times 10^{2}$ min^{-1}
1	0	10.3 (a)	-
2	10	9.0	1.252
3	20	8.0	1.263
4	40	6.5	1.151
5	60	5.5	1.045
6	80	4.5	1.035
7	100	3.5	1.079
		Mean	1.137