CHAPTER-II

PREPARATION, ESTIMATIONS AND EXPERIMENTAL.

PREPARATION, ESTIMATION AND EXPERIMENTAL

These hydrazides were prepared[1] by refluxing equimolar mixtures, of methyl esters of corresponding acids and hydrazine hydrate (80%) in alcohol, on water bath till the reaction is complete. For different hydrazides the time required for completion of reaction is different. Then white crystals of these hydrazides separate out on cooling. These hydrazides were purified by repeated crystallisation. Their purity was checked by observing their physical constants [melting points]. The hydrazides that we have prepared are salicylic acid hydrazide (m.p. 143^{o}C) and O-chloro benzoic acid hydrazide (m.p. 110^{o}C).

The standard solutions for various experiments are prepared as follows :

1) Hydrazides :-

To prepare solutions of [0.025 M] hydrazides, calculated amounts of hydrazides were taken and then these were dissolved in methyl alcohol.

2) Chloramine-T :-

For preparation of this solution, chloramine-T (Fluka A.R.) was used. The calculated amounts of Chloramine-T was dissolved in required quantity of distilled water.

3) Sodium thio-sulphate solution :-

To prepare (0.01 M) this stock solution, 2.480 gms of sodium thio-sulphate (B.D.H., A.R.) was dissolved in one litre distilled water. For the various experiments the desired amount of this stock solution was taken and was diluted to required concentration.

4) Potassium iodide = 5%

5) Sulphuric acid = 1.0 N.

6) Buffer Solution :-

The buffer solutions of different pH were prepared by a known method[2] as follows.

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. The pH of this solution is checked by digital pH meter.

7) Indicator :- Starch solution.

: PROCEDURE :

In a 100 ml standard 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 thermostat till this reaction mixture attains the temperature of thermostat. This reaction starts after addition of Chloramine-T solution. Then 5 ml of chloramine-T solution was added to this reaction mixture. (Total volume of this reaction mixture is 100 ml). After addition of 5 ml of chloramine-T solution, immediately 5 ml aliquot of this reaction mixture was taken and mixed with 5 ml of 5% potassium iodide and 5 ml of 1.0 N sulphuric acid solution which were already taken in iodometric flask. This mixture is allowed to stand for 10 minutes and the liberated iodine was titrated against 0.0005 M sodium thio-sulphate solution, using starch as an indicator. This is an initial reading 'a'. Then after definite time intervals 5 ml aliquots of the reaction mixture were titrated using above procedure. From these titration readings rate constant (k) was calculated.

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

where

a = initial concentration of chloramine-T in terms of 0.0005 M sodium thio-sulphate,

x = amount of Chloramine-T consumed in time interval (t) in terms of 0.0005 M sodium thio-sulphate and

t = time.

: ACTIVATION PARAMETERS :

The above experiment was conducted at different temperatures and rate constants (k) were determined. With the help of this data activation parameters were calculated by using following equations.

1) Energy of Activation (Ea)

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

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

2) Frequency Factor (A)

$$k = Ae^{-Ea/RT}$$

i.e. $\log A = \log k + \frac{Ea}{4.576\ T}$

3) Entropy of Activation ($\Delta S^{\neq}$)

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

Therefore,

$$\Delta S^{\neq} = 4.576 \left[\log k + 10.576 - \log T + \frac{Ea}{4.576\ T} \right]$$

4) Enthalpy $[\Delta H^{\neq}]$

$$\Delta H^{\neq} = Ea - RT$$

5) Free energy $[\Delta G^{\neq}]$

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} .$$

: PRODUCT ANALYSIS :

Detection of p-Toluene-sulphonamide has been done by paper chromatographic method. Benzyl alcohol saturated 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 products of hydrazides (R.CONHNHCOR) were identified by TLC authentic samples prepared according to the literature method. Nitrogen is tested by lime test [3]

REFERENCES

1) Smith, P.A.S. 'Organic Reactions' Vol. III, [Ed. Roger Adam., John Wiley and Sons, Inc. New York] p. 367 (1946).

2) Vogel, A.I., 'A Text Book of Quantitative Inorganic Analysis. [Fourth Edition, Longmans Green & Co. Ltd., London.] (1982).

3) Singh, R.N. Acta Ciencia Indica, Vol. 3, No.4, 320 (1977).

TABLE NO. 2.1.1

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION.

[SAH] = 2.5×10^{-3}M   [$Na_2S_2O_3,5H_2O$] = 5.0×10^{-4}M

[CAT] = 5.0×10^{-4}M   Temperature = 30^oC pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	$k_1 \times 10^4$ min^{-1}
1	0	$10.6_{(a)}$	-
2	5	8.7	6.57
3	10	7.2	6.44
4	15	6.0	6.33
5	20	5.2	5.93
6	25	4.4	5.86
7	30	3.7	5.85
8	35	3.2	5.70
9	40	2.5	5.26

Mean $k_1 \times 10^4 min^{-1}$ = 5.99

TABLE NO. 2.2.1

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION.

[O-CBAH] = 3.0×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

[CAT] = 5.0×10^{-4} M   Temperature = 30^{o}C   pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	k. x 10^4 min^{-1}
1	0	$10.8_{(a)}$	-
2	10	9.9	1.45
3	20	9.1	1.43
4	30	8.4	1.40
5	40	7.8	1.35
6	50	7.2	1.35
7	60	6.7	1.33
8	70	6.3	1.28
9	80	5.9	1.26
10	90	5.5	1.25
11	100	5.2	1.22
12	120	4.5	1.22
13	140	4.0	1.18

Mean k x 10^4 min^{-1} = 1.31

TABLE NO. 2.1.2

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN REAGENT CONCENTRATION.

[SAH] = 2.0×10^{-3}M   [$Na_2S_2O_3,5H_2O$] = 5.0×10^{-4}M

[CAT] = 4.0×10^{-4}M   Temperature = 30^oC pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	$k_1 \times 10^4$ min^{-1}
1	0	10.7(a)	-
2	5	9.4	4.31
3	10	8.3	4.23
4	15	7.4	4.10
5	20	6.6	4.03
6	25	5.9	3.96
7	30	5.3	3.90
8	35	4.8	3.82
9	40	4.3	3.80
10	45	3.9	3.74
11	50	3.5	3.72
12	55	3.2	3.66

Mean $k_1 \times 10^4$ min^{-1} = 3.93

TABLE NO. 2.2.2

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN REAGENT CONCENTRATION.

[O-CBAH] = 2.0×10^{-3}M   [$Na_2S_2O_3, 5H_2O$] = 5.0×10^{-4}M

[CAT] = 4.0×10^{-4}M   Temperature = 30^oC pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	$k \times 10^5$ min^{-1}
1	0	$10.5_{(a)}$	-
2	10	9.9	9.90
3	20	9.4	9.21
4	30	8.9	9.19
5	40	8.5	8.79
6	50	8.1	8.64
7	60	7.7	8.62
8	70	7.4	8.21
9	80	7.1	8.13
10	90	6.8	8.04
11	100	6.5	7.79
12	120	6.0	7.77
13	170	5.0	7.27

Mean $k \times 10^5$ min^{-1} = 8.46

TABLE NO. 2.1.3

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF TEMPERATURE ON THE REACTION.

[SAH] = 1.5×10^{-3}M [$Na_2S_2O_3,5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M Temperature = 50^oC pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	$k_1 \times 10^4$ min^{-1}
1	0	$18.8_{(a)}$	-
2	5	15.3	6.87
3	10	12.5	6.80
4	15	10.2	6.79
5	20	8.4	6.72
6	25	6.9	6.68
7	30	5.7	6.63
8	40	3.9	6.55
9	50	2.7	6.47
10	60	1.5	6.40

Mean $k_1 \times 10^4$ min^{-1} = 6.66

TABLE NO. 2.2.3

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF TEMPERATURE ON THE REACTION.

[O-CBAH] = 1.5×10^{-3}M [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M Temperature = 50^oC pH = 8.88

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

Sr. No.	Time in Minutes(t)	(a - x) ml	k $\times 10^4$ min^{-1}
1	0	$20.8_{(a)}$	-
2	10	17.2	3.16
3	20	14.3	3.13
4	30	11.9	3.10
5	40	9.9	3.09
6	50	8.3	3.06
7	60	7.0	3.03
8	70	5.9	3.00
9	80	5.0	2.97
10	90	4.2	2.96
11	100	3.6	2.92

Mean k $\times 10^4$ min^{-1} = 3.04

TABLE NO. 2.1.4

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN WATER-METHANOL MIXTURE | V/V | AT 30°C

[SAH] = 1.5×10^{-3} M   [$Na_2S_2O_3, 5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M   Temperature = 30°C   pH = 8.88

Medium = Methanol/water (60/40 v/v)

Sr. No.	Time in Minutes(t)	(a - x) ml	$k_1 \times 10^4$ min^{-1}
1	0	$20.2_{(a)}$	-
2	10	17.5	2.39
3	20	15.4	2.26
4	30	14.0	2.04
5	40	12.5	2.00
6	50	11.1	1.97
7	60	10.4	1.84
8	70	9.7	1.75
9	80	8.9	1.71
10	90	8.1	1.69
11	100	7.6	1.63
12	120	6.8	1.51

Mean $k_1 \times 10^4$ min^{-1} = 1.89

TABLE NO. 2.2.4

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN WATER-METHANOL MIXTURE [v/v] AT 30^{o}C.

[O-CBAH] = 1.5 x 10^{-3}M [$Na_2S_2O_3$, $5H_2O$] = 5.0 x 10^{-4}M

[CAT] = 8.0 x 10^{-4}M Temperature = 30^{o}C pH = 8.88

Medium = Methanol/water (20/80 v/v)

Sr. No.	Time in Minutes(t)	(a - x) ml	k x 10^4 min^{-1}
1	0	$17.1_{(a)}$	-
2	10	15.7	1.43
3	20	14.5	1.37
4	30	13.5	1.32
5	40	12.5	1.30
6	50	11.6	1.29
7	60	10.8	1.28
8	70	10.0	1.28
9	80	9.3	1.27
10	90	8.7	1.25
11	100	8.1	1.25
12	120	7.0	1.24
13	140	6.1	1.23
14	160	5.3	1.22

Mean k x 10^4 min^{-1} = 1.27

TABLE NO. 2.2.5

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

EFFECT OF CHANGE IN THE pH OF THE SOLUTIONS.

[O-CBAH] = 1.5×10^{-3}M [$Na_2S_2O_3$,$5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M Temperature = 30^oC pH = 10.8

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

Sr. No.	Time in Minutes(t)	(a - x) ml	k x 10^5 min^{-1}
1	0	$19.3_{(a)}$	-
2	10	18.3	-
3	20	17.4	8.54
4	30	16.6	8.39
5	40	15.9	8.07
6	50	15.3	7.73
7	60	14.9	7.18
8	70	14.5	6.81
9	80	14.0	6.69
10	100	13.0	6.59
11	120	12.0	6.59
12	160	10.3	6.54
13	200	9.0	6.34

Mean k x 10^5 min^{-1} = 7.22

TABLE NO. 2.2.6

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

EFFECT OF THE ADDITION OF SODIUM CHLORIDE ON THE REACTION.

[O-CBAH] = 1.5×10^{-3}M [$Na_2S_2O_3,5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M Temperature = 30^oC pH = 8.88

Medium = Methanol/water (50/50 v/v) [NaCl] = 1.0×10^{-2}M

Sr. No.	Time in Minutes(t)	(a - x) ml	$k \times 10^5$ min^{-1}
1	0	$12.3_{(a)}$	-
2	10	11.7	8.29
3	20	11.2	7.81
4	30	10.8	7.22
5	40	10.4	7.00
6	50	10.0	6.90
7	60	9.6	6.87
8	70	9.3	6.84
9	80	8.9	6.74
10	100	8.2	6.70
11	120	7.6	6.68
12	150	6.8	6.58
13	200	5.6	6.55

Mean $k \times 10^5$ min^{-1} = 7.01