CHAPTER II

PREPARATIONS, ESTIMATIONS

AND

EXPERIMENTAL

CHAPTER -II A

PREPARATIONS:

[A] PREPARATION OF AMIDES :

Preparation of Succinamide[1] : Synthesis of succinamide involves two stages.

a)   Preparation of Diethyl Succinate : A mixture of 58 gms. (0.5 mol) of succinic acid, 81 gms (102.5 ml, 1.76 mol) of absolute ethanol, 190 ml of sodium dried benzene and 20 gm [11ml] of concentrated H_2SO_4 is refluxed for eight hours and poured it into excess of water. Benzene-ester layer was seperated. Aqueous layer was extracted with ether. Benzene and ether extracts are washed combindly with sodium bicarbonate solution until the effervescence cease and again washed with water and dried with anhydrous sodium sulphate. By flash distillation low boiling solvents are removed. Residue was distilled. B.P. of the ester under atomspheric pressure is 217-218°C, yield obtained is 86%.

Ester obtained in this way was added to 25 ml concentrat -ed ammonia solution in a stoppered flask, shaked well for few minutes and allowed to stand for 24 hours. Solid obtained was filtered and washed with a little cold water.

Solid is recrystallised from hot water and then dried in oven. The yield obtained is 88%. Pure succinamide melts at 254°C with decomposition.

b)   BENZAMIDE[2] : Synthesis of benzamide involves following two steps :-

STEP: 1) <u>PREPARATION OF ACID CHLORIDE:</u> Place 0.5 to 1.0 gm of the dry benzoic acid (finely powdered) into a 25 ml flask fitted with a reflux condenser. Add 2.5 to 5.0 ml. of redistilled thionylchloride and reflux gently for 30 minutes. A plug of cotton wool is placed in the top of the condenser to exclude moisture. Rearrange the condenser and distill off the excess of thionyl chloride, (b.p. 78°C). The residue in the flask consists of the acid chloride and can be converted into benzamide.

STEP: 2) <u>PREPARATION OF BENZAMIDE FROM ACID CHLORIDE:</u> (Ammonalysis reaction) — The acid chloride obtained in step one is treated with 20 parts of concentrated ammonia solution (d.0.88) and warmed for a few minutes, if no solid seperates on cooling, evaporate to dryness on a waterbath. Recrystallise the crude amide from water or dilute ethanol. Alternatively stirr the acid chloride with an equivalent weight of ammonium acetate in 10 ml. of acetone at room temperature for one hour. Filter the mixture and evaporate the acetone and crystallise the residual amide from water or dilute ethanol, yield is 80%.

2) <u>PREPARATION OF BAT</u>[3] : It involves two steps —

STEP: 1) <u>PREPARATION OF DBT</u> : Dibromamine-T in tern was obtained by bromination of chloramine-T, Chloramine-T (10gm) is dissolved in 200 ml distilled water and from a burrette, 2 ml of liquid bromine is added with constant stirring of the solution with the help of magnetic stirrer. The golden yellow precipitate of dibromamine-T is obtained which is

thoroughly washed with water, filtered under suction and dried in a vaccum desicater for 24 hours. The purity of the sample was checked by elemental analysis for N, S, Br. (Found N=4.3% S=9.6%, Br=48.5%). The dry sample melts at 92-93°C with decomposition. About 33 gms of DBT is obtained.

STEP: 2) PREPARATION OF BAT: Bromamine-T is obtained by partial debromination of dibromamine-T. Thus DBT prepared (33 gms) is dissolved in small lots at a time and with stirring in 50 ml of aqueous 4 M NaOH. The solution is cooled in ice. Pale yellow crystals of BAT seperate out. They are filtered and washed quickly with very little ice cold water and dried over P_2O_5 . The yield obtained is 84%. The purity of the sample was checked by elemental analysis (found Br=24.4%, N=4.4%, S=0.8%). Purity of the sample is also checked by its spectral data and also iodometrically. The details of spectral data of BAT are given in the Chapter - I Section B (Section B, reference 8).

REAGENT SOLUTIONS:

1] BROMAMINE-T : 3.26 gm of bromamine-T was dissolved in 100 ml of double distilled water. The molarity of this solution is 1.0×10^{-1}M. This solution was found to be stable for more than a fortnight when stored in amber coloured bottle. Still the purity of it is checked iodometrically before the work every day.

2] CHLORAMINE-T: 14.05 gm of A.R. grade chloramine-T was dissolved in 1000 ml of double distilled water. The molarity of this solution is 3×10^{-2} M. This solution was found to be

stable for more than three weeks when stored in amber coloured bottle. Still the purity of it is checked by titrating verses primary standard, ascorbic acid every day, before its use.

3]   ASCORBIC ACID: 8,806 gm of A.R. grade ascorbic acid was dissolved in 1000 ml of double distilled water. The molarity of this solution is 5×10^{-2}M, for stability of the solution 0.05 gm EDTA and 2 gms of formic acid was used. This solution was found to be stable for more than three weeks when stored in amber coloured bottle. But fresh solution was prepared for every week.

4]   BUFFERS: Here sodium carbonate – sodium bicarbonate buffer showing pH 8.88 was used. 1.325 gm Na_2CO_3 was dissolved in 500 ml of double distilled water. The molarity of this solution is 2.5×10^{-2}M. 1.05 gm of $NaHCO_3$ was dissolved in 500 ml of double distilled water. The molarity of the solution was 2.5×10^{-2}M. 10 ml of each in 100 ml reaction mixture show pH = 8.88.

5]   5% POTASSIUM IODIDE: 50 gm of A.R. grade potassium iodide was dissolved in 1000 ml of double distilled water. This makes 5% potassium iodide solution.

6]   2 N HYDROCHLORIC ACID: 178 ml concentrated HCl of analytical grade was diluted with double distilled water to 1000 ml with the help of volumetric flask to prepare 2N HCl solution.

7]   SUCCINAMIDE: 2.92 gms of pure succinamide was dissolved in 400 ml of double distilled water. The molarity of the solution is 5×10^{-2}M. This solution was found to be stable

for more than a fortnight when stored in amber coloured bottle. But for every ten days a fresh stock solution was prepared.

8]   BENZAMIDE: 6.05 gm of benzamide was dissolved in 1000ml of double distilled water. The molarity of the solution is 5×10^{-2} M. This solution was found to be stable for a fortnight when stored in amber coloured bottle. Still for every ten days a fresh stock solution was prepared.

9]   STARCH SOLUTION: Freshly prepared starch solution (BDH Starch) was used everyday.

10]   ALLYL ACETATE: (FLUCA) 1.0012 gms of A.R. grade allyl acetate is dissolved in 200 ml of double distilled water which gives 0.1 M stock solution. Freshly prepared solution was used for the experiments.

11]   PARATOLUENE SULPHONAMIDE (FLUKA): 1.71 gms of A.R. grade paratoluene sulphonamide was dissolved in 100 ml of double distilled water to prepare 0.1 M solution. Freshly prepared solution of paratoluene sulphonamide was used immediately for the experiments.

12]   SODIUM CHLORIDE (BDH) : 0.585 gms of A.R. grade sodium chloride is dissolved in 100 ml of double distilled water and thus freshly prepared 0.1 M solution was immediately used for the experiments.

APPARATUS: All the glass apparatus that are used are varified for the quantities 'O', marked on them. For thermoequillib-riation thermostat with a contact thermometer (of Pharmatrust) is used. pH of the solutions were measured on (Elica Private limited) Model LI-120 pH meter.

CHAPTER- II B

ESTIMATE:

70 ml of the succinamide solution (0.05 mol) was accurately measured and transferred to a well stoppered 250ml standard flask, 10 ml (0.025 mol) sodium bicarbonate and 10 ml (0.025 mol) sodium carbonate buffer solution was added to it. 3 ml distilled water was added to it. Thermostat, was maintained at 70°C . The standard flask containing reaction mixture was kept for 15 minutes in the thermostat to attain the same temperature. Then the flask containing 7 ml. 0.1M BAT was kept seperately in the thermostat to attain the same temperature for 15 minutes and then it was added quickly to the reaction mixture. Just after the addition of BAT,5 ml alliquote of reaction mixture was taken immediately in the iodometric flask. Then at a definite successive time intervals 5 ml alliquotes were taken into the 100 ml iodometric flasks. All these iodometric flasks are kept ready with required amount of ascorbic acid (0.005 mol), 5 ml 5% KI and 5 ml HCl. Freshly prepared starch was used as an indicator. The liberated iodine was measured by using solution of chloramine-T (0.005 mol) with the help of appropriate titrimetric techniques.

A blank experiment was carried out under identical reaction conditions with the substrate i.e. succinamide or benzamide and the result was noticed after 24 hours. Temperature is noted after confirmation, at 8.88 pH.

The pseudo first order rate constants $[k_2\text{obs}]$ were obtained from the plots of $\log \dfrac{a}{(a-x)}$ Vs t in mins where 'a' is the infinite reading of BAT and 'x' is the concentration of BAT at time 't'. The first order rate equation is (2.2)

$$k\ (\text{obs}) = \text{slope} \times 2.303 \qquad\qquad \text{eq.. 2.1}$$

$$k = \frac{2.303}{t}\ \log\ \left(\frac{a}{(a-x)}\right) \qquad\qquad \text{eq..2.2}$$

In case of succinamide this reaction is found to be consecutive irreversible. The 1st step was found to be fast where as step II is slow and rate determining. Rate constants of 2nd step are calculated according to the procedure used for benzamide. The rate constants of first step as well as second step are determined by Swan's time ratio method seperately.

Swan's Time Ratio Method :--

A time ratio method is used for the seperation of k_1 and k_{II} If γ'_1, and γ_2 are the values corresponding to the values c_1 and c_2, which are determined by certain percentage of reaction. Thus the rate $\dfrac{\gamma_2}{\gamma_1}$ is equal to the ratio $\dfrac{t_2}{t_1}$ of the actual times of reaction for these same percentages (Chapter II, Tables 1-8). Values of k (relative) Vs $\dfrac{t_2}{t_1}$ are used to evaluate k (relative), fallowing which a graph for a table of k Vs γ for a certain c will lead to a value of k_I As $K = \dfrac{k_{II}}{k_I}$, k_{II} can be computed.

CHAPTER- II C:

EXPERIMENTAL:

In this section results of some of the kinetic runs are given The short forms that are used here are as follows:-

BAT	:	Bromamine-T
SAD	:	Succinic acid diamide.
PTS	:	Paratoluene Sulphonamide
AA	:	Ascorbic Acid
CAT	:	Chloramine-T

k_1 and k_2 [SAD] = Calculated by time ratio method

TABLE - II- 1

Effect of change in substrate concentration on the oxidation of succinic acid diamide by Bromamine-T.

[AA] = 5 x 10^3M   [SAD] = 1.7 x 10^{-2}M.

[CAT] 5 x 10^3M   [BAT] = 2.0 x 10^{-2}M.

Temperature = 70°C   pH = 8.88

Sr. No	Time in min.	a-x	$\log \frac{a}{a-x}$	k_1x10^{-2} min^{-1}	k_2x10^{-2} min^{-1}	k by first order x 10^{-2}min.
1	05	17.0	0.0705	6.46	3.22	3.24
2	10	15.1	0.1220	5.58	2.79	2.80
3	15	13.7	0.1643	5.02	2.51	2.52
4	20	12.5	0.2041	4.68	2.34	2.35
5	30	11.1	0.2403	3.67	1.81	1.84
6	40	10.4	0.2839	3.25	1.63	1.63
7	50	9.5	0.3233	2.95	1.48	1.48
8	60	8.9	0.3516	2.67	1.34	1.34
9	75	8.0	0.3979	2.43	1.22	1.22
10	90	7.3	0.4377	2.23	1.12	1.12

Mean k_{cal} = 1.95 x 10^{-2} min^{-1} k_{graph} = 1.96 x 10^{-2}Min^{-1}

k_2 by first order = 1.95 x 10^{-2} min^{-1}

TABLE - II -2

Effect of change in substrate concentration on the oxidation of benzamide by Bromamine-T.

$[AA]$ = $5 \times 10^{-3} M$ $[BENZAMIDE]$ = $3.0 \times 10^{-2} M$

$[CAT]$ = $5 \times 10^{-3} M$ $[BAT]$ = $3.0 \times 10^{-3} M$

Temp. = $70°C$ pH = 8.88

Sr.No	Time of Mins.	a-x	log a/a-x	$k \times 10^{-1} min^{-1}$
1.	6	13.4	0.5026	1.93
2.	8	13.7	0.6410	1.85
3.	10	13.9	0.7659	1.76
4	12	14.0	0.8451	1.62
5	15	14.1	0.9420	1.45
6	18	14.2	1.0669	1.37
7	21	14.3	1.2430	1.36
8	25	14.4	1.5441	1.42

mean k = 1.59×10^{-1} min^{-1}

k_{graph} = 1.54×10^{-1} min^{-1}

TABLE-II 3

Effect of change in concentration of Bromamine-T on the oxidation of Succinic acid diamide by Bromamine-T.

$[AA]$ = $5 \times 10^{-3}M$ $[SAD]$ = $2 \times 10^{-2}M$

$[CAT]$ = $5 \times 10^{-3}M$ $[BAT]$ = $2.4 \times 10^{-2}M$

Temp. = $70°C$ pH = 8.88

Sr. No	Time in min.	a-x	$\log \dfrac{a}{a-x}$	$k_1 \times 10^{-2}$ min.$^{-1}$	$k_2 \times 10^{-2}$ min^{-1}	k by first order $\times 10^{-2}$ min^{-1}
01	05	20.6	0.0497	4.545	2.27	2.28
02	10	18.2	0.1035	4.744	2.37	2.38
03	15	16.2	0.1540	4.700	2.35	2.36
04	20	14.6	0.1992	4.560	2.28	2.29
05	30	12.7	0.2598	3.970	1.98	1.99
06	40	11.2	0.3143	3.590	1.79	1.80
07	50	10.1	0.3592	3.290	1.64	1.65
08	60	8.7	0.4240	3.220	1.61	1.62
09	70	7.8	0.4715	3.090	1.54	1.55
10	90	6.6	0.5440	2.770	1.39	1.39
11	110	5.3	0.6393	2.650	1.33	1.33
12	130	4.6	0.7008	2.470	1.24	1.24

Mean k = 1.80×10^{-2} min^{-}

k_2 by time

ratio method= 1.79×10^{-2}min^{-1}

k_{graph} = 1.60×10^{-2} min^{-1}

TABLE- II - 4

Effect of change in concentration of Bromamine-T on the oxidation of
of Benzamide by Bromamine-T.

[AA] = 5×10^{-3}M   [Benzamide] = 3×10^{-2}M

[CAT] = 5×10^{-3}M   [BAT] = 4×10^{-3}M

Temp. = 70°C   pH = 8.88

Sr. No.	Time in mines	a-x	log a/a-x	$k \times 10^{-1} min^{-1}$
01	3	2.3	0.2717	2.09
02	4	2.0	0.3324	1.91
03	5	1.7	0.4030	1.86
04	6	1.4	0.4873	1.87
05	7	1.2	0.5543	1.82
06	8	1.0	0.6335	1.82
07	9	0.9	0.6792	1.74
08	10	0.8	0.7304	1.68
09	12	0.6	0.8553	1.64
10	15	0.5	0.9345	1.49
11	18	0.3	1.1563	1.48
12	21	0.2	1.3324	1.46
13	25	0.1	1.6325	1.50

mean k = $1.72 \times 10^{-1} min^{-1}$

k_{graph} = $1.53 \times 10^{-1} min^{-1}$

TABLE-II - 5

Effet of addition of paratoluene sulphonamide on the oxidation of Succinic acid diamide by Bromamine-T.

$[AA] = 5 \times 10^{-3}M$ $[SAD] = 3.5 \times 10^{-2}M$

$[CAT] = 7 \times 10^{-3}M$ $[BAT] = 7.0 \times 10^{-3}M$

Temp. $= 70°C$ $[PTS] = 7.0 \times 10^{-3}M$

                           pH $= 8.88$

Sr. No	Time in min.	a-x	log a/a-x	$k_1 \times 10^{-2}$ min^{-1}	$k_2 \times 10^{-2}$ min^{-1}	k by first order $\times 10^{-2}$ min^{-1}
01	9	3.7	0.2769	14.130	7.07	7.09
02	12	3.1	0.3537	13.530	6.77	6.79
03	15	2.7	0.4137	12.680	6.34	6.35
04	18	2.5	0.4472	11.402	5.70	5.72
05	22	2.2	0.5027	10.480	5.24	5.26
06	27	1.9	0.5663	9.660	4.83	4.83
07	32	1.6	0.6410	9.189	4.59	4.61
08	38	1.3	0.7312	8.830	4.42	4.43
09	44	1.0	0.8451	8.810	4.41	4.62
10	50	0.9	0.8909	8.172	4.09	4.10

Mean k $= 5.36 \times 10^{-2}$ min^{-1}

$k_{graph} = 5.18 \times 10^{-2}$ min^{-1}

TABLE II 6

Effect of addition of paratoluene sulphonamide on the oxidation of Benzamide by Bromamine-T.

[AA]   =   5 x 10^{-3}M   [Benzamide] =   3 x 10^{-2}M.

[CAT] =   5 x 10^{-3}M   [BAT]   =   3 x 10^{-3}M

Temp. =   70°C   [PTS]   =   6x 10^{-3}M

                                   pH   =   8.88

Sr. No	Time in mins	a - x	log a/a-x	$k \times 10^{-1} min^{-1}$
1	4	13.1	0.3979	2.29
2	6	13.4	0.5026	1.92
3	8	13.7	0.6410	1.84
4	10	13.9	0.7659	1.76
5	12	14.0	0.8451	1.62
6	15	14.1	0.9420	1.44
7	18	14.2	1.0669	1.36
8	21	14.3	1.2430	1.36
9	25	14.4	1.5440	1.42

mean k   =   1.67 x $10^{-1} min^{-1}$

k_{graph} =   1.53 x $10^{-1} min^{-1}$

<u>TABLE-II - 7</u>

Effect of change in temperature on the oxidation of Succinic acid diamide by Bromamine-T

$[AA] = 5 \times 10^{-3}M$ $[SAD] = 3.5 \times 10^{-2}$

$[CAT] = 5 \times 10^{-3}M.$ $[BAT] = 7.0 \times 10^{-3}$

$Temp. = 65°C$ $pH = 8.88$

Sr. No	Time in min.	a-x	log a/a-x	$k_1 \times 10^{-2} min^{-1}$	$k_2 \times 10^{-2} min^{-1}$	k by, first order x $10^2 min^1$
1	7	4.7	0.1730	11.340	5.67	5.69
2	10	4.3	0.2116	9.707	4.85	4.87
3	15	3.5	0.3010	9.209	4.60	5.62
4	20	3.0	0.3679	8.432	4.22	4.23
5	25	2.6	0.4301	7.893	3.95	3.96
6	33	2.4	0.4648	6.458	3.23	3.24
7	40	2.2	0.5026	5.761	2.88	2.89
8	50	1.8	0.5898	5.400	2.70	2.71
9	65	1.4	0.6989	4.920	2.46	2.47
10	80	1.2	0.7659	4.385	2.19	2.20

Means k $= 3.68 \times 10^{-2} min^{-1}$

k_2 by time ratio method $= 3.67 \times 10^{-2} min^{-1}$

$k_{graph} = 3.62 \times 10^{-2} min^{-1}$

TABLE - II - 8

Effect of change in temperature on the oxidation of Benzamide by Bromamine-T

$[AA] = 5 \times 10^{-3}M$ $[Benzamide] = 3 \times 10^{-2}M$

$[CAT] = 5 \times 10^{-3}M$ $[BAT] = 3 \times 10^{-3}M$

Temp. $= 65°C$ pH $= 8.88$

Sr. No	Time in mins	a - x	log a/a-x	$k \times 10^{-1} min^{-1}$
1	4	12.6	0.2653	1.53
2	6	13.0	0.3680	1.41
3	8	13.3	0.4649	1.34
4	10	13.4	0.5027	1.16
5	12	13.5	0.5440	1.04
6	15	13.7	0.6410	0.98
7	18	13.9	0.7659	0.98
8	21	14.0	0.8451	0.93
9	25	14.1	0.9420	0.87
10	35	14.2	1.0669	0.70

mean k $= 1.09 \times 10^{-1} min^{-1}$

$k_{graph} = 1.32 \times 10^{-1} min^{-1}$

CHAPTER-II D

The end products of these oxidation reactions are paratoluene sulphonamide, corresponding acids called succinic acid and benzonic acid and ammonia. Paratoluene sulphonamide was detected by paper chromatography[5]. Here benzil alcohol saturated with water was used as a solvent with 0.5% vanilline in 1% HCl solution in ethanol as a spray reagent.

Succinic acid and benzoic acid obtained are identified by usual, standard laboratory tests after finding of their chromatographic seperations. They are confirmed by their melting points. Their melting points are found to be 158°C and 121°C respectively which are exactly matching as given in the literature.

Ammonia evolved at the time of reaction can not be detected by its smell as the concentration of amides that are taken in the reactions are quite small. This evolution of ammonia is tested and confirmed by the wet termmeric paper which changes
from yellow to red when kept over the reaction mixture for a long time.

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