CHAPTER II

PREPARATIONS, ESTIMATIONS

AND

EXPERIMENTAL

(A) PREPARATIONS :

Both malonic acid dihydrazide and succinic acid dihydrazide were prepared by a well known method which has two steps.
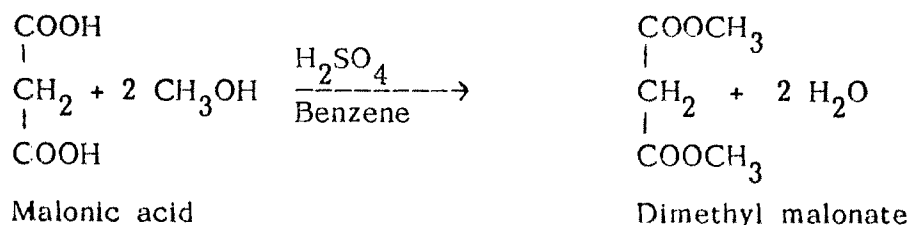
Step - I : Preparation of ester from corresponding acids[1]
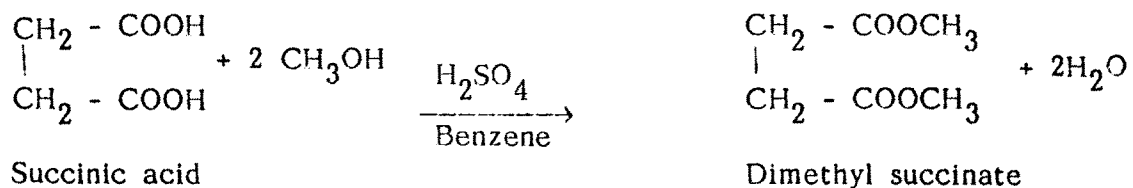
In a 1000 ml round bottom flask a mixture of 58 gms of succinic acid (52 gms of malonic acid) (Both BDHAR), 102.5 ml absolute methyl alcohol (SRL) 190 ml benzene (E.Merk A.R.) and 11 ml sulphuric acid (E Merk A.R.) were refluxed for 8 hours in case of succinic acid and 10 hours in case of malonic acid in hot water bath. Then these reaction mixtures were poured into excess of cold water. Then benzene-ester layer and aqueous ester layer were separated with the help of separating funel. Benzene ester layers were extracted with ether and washed with 5% sodium bicarbonate till all the effervescences ceases and finally with water. Aqueous ester layers were extracted with ether. These two ether layers having benzene and esters are mixed together. Then ether was removed by evapcration and benzene by distillation which gives these two eters. Dimethyl succinate was collected at $196^{O}C$ and dimethyl malonate was collected at $178^{O}C$ so as to get them in pure form.

These two esters were purified by repeated distillation at their corresponding boiling points,

Dimethyl malonate b.p. $178^{O}C$

Dimethyl succinate b.p. $196^{O}C$

$$\begin{array}{ccc} \text{COOH} & & \text{COOCH}_3 \\ | & & | \\ \text{CH}_2 + 2\text{ CH}_3\text{OH} & \xrightarrow[\text{Benzene}]{\text{H}_2\text{SO}_4} & \text{CH}_2 + 2\text{ H}_2\text{O} \\ | & & | \\ \text{COOH} & & \text{COOCH}_3 \end{array}$$

Malonic acid   Dimethyl malonate

$$\begin{array}{l} CH_2 - COOH \\ | \\ CH_2 - COOH \end{array} + 2\ CH_3OH \quad \xrightarrow[\text{Benzene}]{H_2SO_4} \quad \begin{array}{l} CH_2 - COOCH_3 \\ | \\ CH_2 - COOCH_3 \end{array} + 2H_2O$$

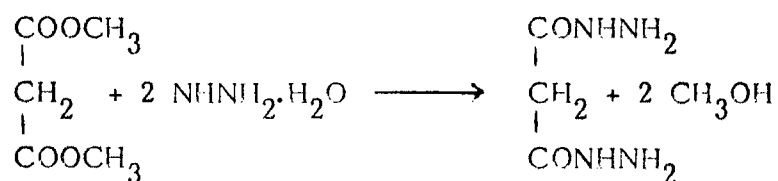Succinic acid   Dimethyl succinate

Step - II : Preparation of Dihydrazides[1,2]

In a 250 ml round bottom flask fitted with a reflux condenser in hot water bath, 15 ml of hydrazine hydrate (80% Thomas Baker A.R.) was added, to this solution. Then 15 ml of dimethyl ester was added dropwise and the mixture was heated under reflux. (15 min. for dimethyl succinate and 2 hour for dimethyl malonate). Absolute methanol was added to this reaction mixture till a clear solution is obtained and refluction was continued for 3 hr so as to purify the compounds. When alcohol was distilled off a fine crystals of dihydrazides were obtained. Both dihydrazides were crystallised from methanol and to purify it repeated crystallisation technique is utilised.
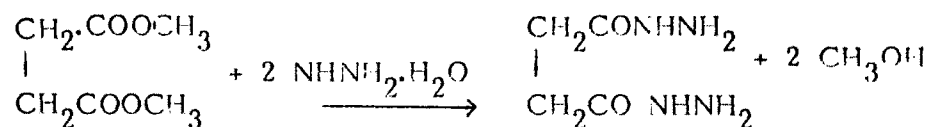
The purity of these two dihydrazides were checked by their melting points and TLC.

      M.P. of malonic acid dihydrazide   = $155^{O}C$

and   M.P. of succinic acid dihydrazide   = $167^{O}C$

$$\begin{array}{l} COOCH_3 \\ | \\ CH_2 \\ | \\ COOCH_3 \end{array} + 2\ NHNH_2 \cdot H_2O \quad \longrightarrow \quad \begin{array}{l} CONHNH_2 \\ | \\ CH_2 \\ | \\ CONHNH_2 \end{array} + 2\ CH_3OH$$

Malonic acid dihydrazide

$$\begin{array}{l} CH_2 \cdot COOCH_3 \\ | \\ CH_2COOCH_3 \end{array} + 2\ NHNH_2 \cdot H_2O \quad \longrightarrow \quad \begin{array}{l} CH_2CONHNH_2 \\ | \\ CH_2CO\ NHNH_2 \end{array} + 2\ CH_3OH$$

Succinic acid dihydrazide

The standard solutions for various experiments were prepared by using doubly distilled water as follows.

1) Dihydrazides :

Stock solution of these two dihydrazides were parepared by following procedure.

The 0.1 M stock solutions of dihydrazides were prepared by dissolving 1.321 g of malonic acid dihydrazide and 1.461 g of succinic acid dihydrazide in 100 mls of doubly distilled water.

2) Chloramine-T :

Chloramine-T (Lobha AR) free from dichloramine-T contaminants was always kept in vacuum desicater ($CaCl_2$). The 0.01 M stock solution was prepared by dissolving 0.2817 g of chloramine-T in 100 ml doubly distilled water and it is kept in amber colored bottle.

3) Sodium thiosulphate : (E Merk AR)

To prepare 0.01 M stock solution 2.482 g $Na_2S_2O_3.5H_2O$ were dissolved in 1000 ml doubly distilled water.

4) Buffer Solution :

a) Sodium bicarbonate (0.025 M)

To prepare 0.025 M sodium bicarbonate solution 0.025 gms of sodium bicarbonate (SRL) was dissolved in 250 ml doubly distilled water.

b) Sodium Carbonate (0.025 M)

To prepare 0.025 M sodium carbonate solution 0.662 gms of sodium carbonate (SRL) was dissolved in 250 ml doubly distilled water.

The mixture of 10 ml sodium bicarbonate (0.025 M) and 10 ml

sodium carbonate (0.025 M) is added in a reaction mixture and pH was counted on digital pH meter and it was found to be 9.0.

5) Potassium Iodide : (5%)

Always freshly prepared potassium iodide solution was used. To prepare 5% solution 50 g of potassium iodide (BDH) was dissolved in 1000 ml doubly distilled water.

6) Sulphuric Acid : (1 N)

27.6 mls of AR quality H_2SO_4 when dissolved in 1000 ml doubly distilled water it gives 1 N (approx.) solution.

7) Starch : (Indicator)

Everyday freshly prepared starch solution was used, starch (BDH).

All other reagents used were of AR grade Allyl acetate (Fluka), Methanol (SRL), p-Toluene sulphonamide (Fluka), sodium chloride (BDH) and doubly distilled water were used throughout all the experiments.

(B) ESTIMATIONS[3] :

A 10 ml dihydrazide solution was accurately measured and trans-ferred to a well stoppered 250 ml standard flask and 20 ml buffer solution (10 ml sodium bicarbonate (0.025 M) and 10 ml sodium carbonate (0.025 M)) and 60 ml double distlled water were added to it. When this mixture attains the required temperature in a thermostated water bath, 10 ml solution of chloramine-T (CAT) which has been already kept in the same thermostat to attain the required temperature was added to this reaction

mixture. The reaction was then followed by taking 5 ml reaction mixture by pipette and pouring it into 100 ml iodimetric flask in which 5 ml of 5% KI solution and 5 ml 1 N sulphuric acid solution, were already kept. This mixture was allowed to stand for 10 minutes and then the liberated iodine was estimated with standard 0.0005 M sodiumthiosulphate solution using starch as an indicator.

A blank experiment was performed under identical conditions without dihydrazide. It was found that there is no decomposition of chloramine-T at these experimental conditions.

The first order rate constants $k_{(obs)}$ were obtained from the plots of log (a-x) versus time 't' in minutes where 'a' is the initial concentration of CAT and x is the CAT concentration at time 't'.

The rate constant k is obtained by following equation

$$k_{(obs)} = - \text{slope} \times 2.303 \qquad \qquad ... (2.1)$$

Various rate constant values are also calculated by a following standard equation

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

Swain's Time Ratio Method[8,9] :

A Swain's time ratio method is used for separation of the rate constants k_1 and k_2 for these consecutive irreversible reactions. If Υ_1 and Υ_2 are the values of Υ corresponding to the s_1 and s_2, which are determined by certain percentage of reaction. The Υ_2/Υ_1 ratio is equal to the ratio t_2/t_1 of the actual times of reaction for these same percentages. The graph or a table of values of $K_{(relative)}$ versus t_2/t_1 can be used to

evaluate $K_{(relative)}$, following which a graph or a table of K versus $\mathcal{T}$ for a certain δ will lead to a value of k_1. As $K_{(relative)} = k_2/k_1$ can be computed.

PRODUCT ANALYSIS

Among the reaction products p-toluene sulphonamide was detected by the paper chromatography[4] using following method. Benzyl alcohol and water was used as a solvent 0.5% vanillin in 1% hydrochloric acid solution in ethanol was used as spraying reagent. R_f value was found to be 0.91. The dicarboxylic acids, malonic acid and succinic acid were detected by paper chromatography[5] using following method and also by spot tests.[6] The mixture of ethanol in proportion with ammonia and water 80:4:16 were used as solvent and methyl red is used as a spraying reagent. R_f values were found to be 0.26 for malonic acid and 0.28 for succinic acid. p-Toluene sulphonamide (PTS) and dicarboxylic acids were also detected by TLC. Nitrogen was tested by lime test.[7]

REFERENCES

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2) P.A.S.Smith, "Organic Reactions", John Wiley, London, 1946, 367.

3) J.Coull, H.B.Hope and B.Gouguell, J. Amer. Chem. Soc., 1935, 57, 1489.

4) B.T.Gowda and B.S.Sherigara, Int. J. Chem. Kinet, 1989, 21(1), 31.

5) F.Lederer and M.Lederer,"Chromatography," Elsevier, London, 1957, 197.

6) F.Feigl,"Spot Tests in Organic Analysis," Elsevier, Amsterdam, 1956, 120.

7) R.N.Sing, Acta Cineca, Indica, 1977, 3, 320.

8) A.A.Frost and R.G.Pearsin, "Kinetics and Mechanism", Wiley Estern University, 1970, 171.

9) C.G.Swain, J. Am. Chem. Soc., 1944, 66, 1696.

(C) EXPERIMENTAL :

In this section results of some of the kinetic runs are given. The short forms that are used throughout this dissertation are given below :

CAT	:	Chloramine-T
MAD	:	Malonic Acid Dihydrazide
SAD	:	Succinic Acid Dihydrazide
k	:	First order rate constant obtained by calculation using equation 2.2
$k_{(graph)}$	:	First order rate constant obtained by graph of log(a-x) vs 't'
k_1 & k_2	:	Rate constants separated by Swain's time ratio method as discussed earlier in this topic.
PTS	:	p-toluene sulphonamide

TABLE - 2.1

EFFECT OF CHANGE IN THE SUBSTRATE CONCENTRATION
ON THE OXIDATION OF MAD BY CAT

$[MAD] \times 10^4 = 7.0$ M $\qquad\qquad [CAT] \times 10^3 = 1.0$ M

$\qquad$ pH $= 9.0$ $\qquad\qquad\qquad\qquad$ TEMP $= 30^{\circ}$C

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^5 s^{-1}$	$k_1 \times 10^5 s^{-1}$	$k_2 \times 10^5 s^{-1}$
1	0	20.0	-	-	-
2	10	18.9	9.404	18.75	9.375
3	20	18.0	8.780	17.50	8.752
4	30	17.1	8.701	17.34	8.674
5	40	16.3	8.523	16.99	8.495
6	50	15.5	8.485	16.92	8.459
7	60	14.8	8.365	16.67	8.338
8	75	13.7	8.414	16.78	8.389
9	90	12.7	8.406	16.76	8.381
10	105	11.8	8.375	16.70	8.350
11	120	11.0	8.016	15.90	7.992
12	140	10.0	8.252	16.45	8.227
13.	160	9.1	8.201	16.35	8.177
14	180	8.3	8.142	16.23	8.116
15	200	7.6	8.061	16.07	8.035

$\qquad\qquad\qquad$ Mean $=$ $\quad$ 8.458 $\qquad$ 16.86 $\qquad$ 8.433

$\qquad\qquad\qquad$ $k_{(graph)}$ $\quad$ 8.291

TABLE - 2.2

EFFECT OF CHANGE IN THE SUBSTRATE CONCENTRATION
ON THE OXIDATION OF SAD BY CAT

[SAD] x 10^4 = 8.0 M $\qquad\qquad$ [CAT] x 10^3 = 1.0 M

$\qquad$ pH = 9.0 $\qquad\qquad\qquad\qquad$ TEMP. = 30^0C

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	20.0	-	-	-
2	5	17.8	3.860	7.696	3.848
3	10	16.1	3.718	7.538	3.769
4	15	14.4	3.653	7.283	3.641
5	20	12.9	3.651	7.229	3.639
6	25	11.7	3.571	7.120	3.560
7	30	10.5	3.570	7.118	3.559
8	35	9.5	3.543	7.064	3.532
9	40	8.6	3.516	7.010	3.505
10	50	7.0	3.498	6.974	3.487
11	60	5.9	3.396	6.771	3.335
12	70	4.8	3.388	6.755	3.377
13	80	4.0	3.353	6.685	3.342
14	90	3.4	3.280	6.539	3.269
		Mean $k_{(graph)}$	3.542 3.506	7.062	3.531

TABLE - 2.3

EFFECT OF CHANGE IN CONCENTRATION OF CHLORAMINE-T ON THE OXIDATION OF MAD BY CAT

$[MAD] \times 10^4 = 1.0$ M $[CAT] \times 10^4 = 14.0$ M

pH $= 9.0$ TEMP $= 30^{\circ}$C

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	28.0	–	–	–
2	10	25.9	1.297	2.586	1.293
3	20	24.1	1.249	2.490	1.245
4	30	22.4	1.239	2.470	1.235
5	40	20.8	1.234	2.460	1.230
6	50	19.3	1.238	2.468	1.234
7	60	18.1	1.211	2.414	1.207
8	75	16.2	1.215	2.422	1.211
9	90	14.6	1.204	2.406	1.200
10	105	13.1	1.205	2.402	1.201
11	120	11.8	1.200	2.392	1.196
12	140	10.2	1.202	2.396	1.198
13	160	8.9	1.193	2.378	1.189
14	180	7.8	1.183	2.358	1.179
15	200	6.9	1.166	2.225	1.112
		Mean	1.219	2.426	1.213
		$k_{(graph)}$	1.190		

TABLE - 2.4

EFFECT OF CHANGE IN CONCENTRATION OF CHLORAMINE-T ON THE OXIDATION OF SAD BY CAT

$[SAD] \times 10^4 = 5.0$ M $\qquad\qquad$ $[CAT] \times 10^4 = 18.0$ M

$\qquad$ pH $= 9.0$ $\qquad\qquad\qquad\qquad$ TEMP $= 30^{\circ}C$

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	36.0	-	-	-
2	5	33.5	2.398	4.781	2.390
3	10	31.3	2.332	4.649	2.324
4	15	29.3	2.286	4.557	2.278
5	20	27.4	2.273	4.332	2.216
6	30	24.0	2.251	4.488	2.244
7	40	21.1	2.225	4.436	2.218
8	50	18.5	2.218	4.422	2.211
9	60	16.2	2.216	4.418	2.209
10	70	14.2	2.213	4.412	2.206
11	80	12.5	2.203	4.392	2.196
12	90	11.2	2.261	4.508	2.254
13	100	10.0	2.163	4.312	2.156
		Mean	2.236	4.458	2.229
		k(graph)	2.175		

TABLE - 2.5

EFFECT OF TEMPERATURE ON THE OXIDATION

OF MAD BY CAT

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 45°C

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	20.0	-	-	-
2	5	17.6	4.252	8.477	4.238
3	10	15.5	4.245	8.463	4.231
4	15	13.7	4.173	8.320	4.160
5	20	12.2	4.118	8.210	4.105
6	25	10.9	4.045	8.065	4.032
7	30	9.7	4.018	8.012	4.005
8	35	8.7	3.961	7.879	3.948
9	40	7.8	3.923	7.821	3.910
10	45	7.0	3.888	7.752	3.876
11	50	6.3	3.850	7.676	3.838
12	60	5.0	3.852	7.680	3.840
13	70	4.0	3.832	7.640	3.820
14	80	3.2	3.818	7.612	3.806
15	90	2.6	3.778	7.532	3.766
		Mean	3.982	7.939	3.950
		$k_{(graph)}$	3.882		

TABLE - 2.6

EFFECT OF TEMPERATURE ON THE OXIDATION
OF SAD BY CAT

$[SAD] \times 10^4 = 5.0$ M $[CAT] \times 10^3 = 1.0$ M

pH $= 9.0$ TEMP $= 45^{\circ}C$

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	20.0	-	-	-
2	5	16.0	7.436	14.82	7.413
3	10	12.8	7.435	14.82	7.413
4	15	10.3	7.371	14.69	7.948
5	20	8.3	7.328	14.61	7.305
6	25	6.7	7.290	14.53	7.264
7	30	5.5	7.172	14.29	7.949
8	35	4.4	7.210	14.37	7.187
9	40	3.5	7.262	14.47	7.239
10	45	3.0	7.025	14.06	7.003
11	50	2.4	7.067	14.09	7.045
12	55	2.0	6.976	13.90	6.945
		Mean	7.233	14.42	7.210
		k(graph)	7.043		

TABLE - 2.7

EFFECT OF CHANGE IN pH ON THE OXIDATION

OF MAD BY CAT

$[MAD] \times 10^3 = 1.0$ M $\qquad$ $[CAT] \times 10^3 = 1.0$ M

$\qquad$ pH $= 7.55$ $\qquad\qquad\qquad$ TEMP. $= 30^{\circ}$C

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^4 s^{-1}$	$k_1 \times 10^4 s^{-1}$	$k_2 \times 10^4 s^{-1}$
1	0	19.0	-	-	-
2	5	17.0	3.707	7.391	3.695
3	10	15.3	3.610	7.197	3.598
4	15	13.9	3.472	6.922	3.461
5	20	12.6	3.422	6.822	3.411
6	25	11.4	3.405	6.789	3.394
7	3C	10.3	3.400	6.779	3.389
8	35	9.4	3.350	6.679	3.339
9	40	8.5	3.350	6.679	3.339
10	50	7.0	3.328	6.635	3.317
11	60	5.7	3.343	6.665	1.332
12	70	4.7	3.325	6.629	3.314
13	80	3.9	3.298	6.675	3.287
14	90	3.3	3.242	6.404	3.232
15	100	2.8	3.197	6.374	3.187
		Mean	3.389	6.757	3.378

TABLE - 2.8

EFFECT OF CHANGE IN pH ON THE OXIDATION

OF SAD BY CAT

$[SAD] \times 10^4 = 5.0$ M $\qquad$ $[CAT] \times 10^3 = 1.0$ M

$\qquad$ pH $= 10.54$ $\qquad\qquad$ TEMP $= 30^\circ C$

Sr. No.	Time in min.(t)	(a-x)	$k \times 10^5 s^{-1}$	$k_1 \times 10^5 S^{-1}$	$k_2 \times 10^5 S^{-1}$
1	0	19.4	-	-	-
2	10	18.5	7.917	15.78	7.892
3	20	17.7	7.641	15.23	7.617
4	30	17.0	7.336	14.63	7.313
5	40	16.3	7.253	14.46	7.231
6	50	15.7	7.053	14.06	7.031
7	60	15.2	6.776	13.51	6.755
8	75	14.6	6.316	12.59	6.296
9	90	13.8	6.306	12.57	6.286
10	105	13.1	6.888	13.73	6.866
11	120	12.5	6.103	12.16	6.084
12	140	11.8	5.918	11.79	5.899
13	160	11.1	5.815	11.59	5.797
14	180	10.5	5.683	11.33	5.665
15	200	9.8	5.690	11.34	5.672
	Mean :		6.621	13.20	6.600