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George W. Engstrom

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THE CONDENSATION OF PHENOLS WITH MALEIC ANNHYDRIDE

By

George W. Engstrom

This thesis is approved as a creditable independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation for the guidance and able assistance given so generously by Dr. V. S. Webster, Head of the Chemistry Department at South Dakota State College, without which, this thesis would have been impossible.

Introduction

The condensation of phenols with phthalic anhydride to give acid-base indicators is well known. Baeyer (1) first reported the preparation of phenolphthalein in 1871 using concentrated sulfuric acid as the catalyst. The successful use of stannic chloride as the catalyst for the preparation of phenolphthalein was reported by Baeyer (2) in 1880.

Early reports of the condensation of resorcinol (3), p-chlorophenol (4) and o-cresol (5) with phthalic anhydride have also been made. The reaction of phenols with coumarin (6), with diphenic acid anhydride (7) and with succinic anhydride (8) to form compounds comparable in structure to the phthaleins has been reported.

Dass and Tewari (9) reported the preparation of maleins of pyrocatechol, pyrogallol, o-cresol, 2-naphthol, m-aminophenol and phenylenediamine. Similar results were reported by Sisson (10) who prepared several maleins and succinsins from phenols with maleic anhydride and succinic anhydride respectively. These had indicator properties but were not pure compounds.

Mehrotra, Tewari, and Dube (11) reported the preparation of resorcinol-succinein and its use as an adsorption indicator in argentometric titrations. Webster and Kamstra (12) prepared and purified phenolmalein, resorcinolmalein and p-bromophenolmalein.

It seemed of interest to prepare a series of related phenolmaleins to see what different properties would result if the position of the group (ortho, meta and para) on the phenol ring were changed and also if the group (chlorine, bromine and iodine) were changed.

This problem was initiated by preparing a known product, p-bromophenolmalein, following the procedure used by Webster and Kamstra (12). It was thought that this would bring to light difficulties which might be encountered in the preparation of similar acid-base indicators.

<u>Preparation and purification of the test product</u>: (p-bromophenolmalein)

A mixture of fifteen grams of maleic anhydride, fifty three grams of p-bromophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 130-135° C for twelve hours with frequent stirring. The reaction mixture was placed in about six hundred milliliters of distilled water and steam distilled for one hour to remove any unreacted phenol.

The liquid which remained in the flask was cooled to room temperature, filtered and the product extracted with ether. The ether was evaporated on the steam bath. The solid residue was recrystallized from an alcohol-carbon tetrachloride solution according to the procedure reported by Webster and Kamstra (12).

The solid was dissolved in acetone to make a five per cent solution and this solution was then allowed to run through a chromatographic column with Merck alumina as the adsorbent. The column developed several layers, each representing a different compound. After extruding the column, it was found that the red colored layer at the lower end of the column was the indicator compound. It was eluted from the alumina with a ten per cent alcohol-water solution and filtered. The solution was evaporated on the steam bath leaving the solid indicator compound. The compound was dried in a desiccator with calcium chloride as the drying agent. The indicator compound was dark red in color.

This solid blackened at 195-200° C but did not melt below 305° C. The indicator compound was colorless in acid and red in basic solution. The pH range was found to be 5.3-7.2 . Webster and Kamstra (12) reported the compound as colorless in acid and straw colored in basic solution and having a pH range of 8.5 - 10.5 . They reported a melting point of 188-190° C and no color for the solid compound.

Theoretical bromine for $C_{16}H_{10}O_4Br_2$ 37.51 per cent.

Bromine found 36.34 per cent.

Theoretical molecular weight for p-bromophenolmalein 426.07 .

Molecular weight found 418.00.

Preparation and purification of original products:

p-chlorophenolmalein-

A mixture of fifteen grams of maleic anhydride, forty grams of p-chlorophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 150-160° C for twelve hours with frequent stirring. The reaction mixture was placed in about six hundred milliliters of distilled water and steam distilled for one hour to remove any unreacted phenol.

The liquid which remained in the flask was cooled to room temperature, filtered and the product extracted with ether. The ether was evaporated on the steam bath and the resulting solid was recrystallized from alcohol-carbon tetrachloride solution according to the procedure reported by Webster and Kamstra (12).

To assure maximum purity, this solid was dissolved in petroleum ether and allowed to run through a chromatographic column with Merck alumina as the adsorbent. After extruding the column, it was found that the orange colored layer at the lower end of the column was the indicator compound. It was eluted from the alumina with ten per cent alcohol-water solution and filtered. Not all the adsorbed indicator was eluted from the alumina with the alcohol-water solution so a dilute ammonium hydroxide solution was used to take off the remaining indicator. The alcohol-water solution was evaporated on the steam bath leaving the solid indicator compound. The alkaline solution was made slightly acid with dilute hydrochloric acid and evaporated on the steam bath. Since hydrochloric acid was added to the ammonium salt of the indicator, some ammonium chloride was mixed with the solid. The indicator was dissolved in ether leaving the ammonium chloride undissolved. The ether solution of the indicator was evaporated on the steam bath leaving the solid product.

The compound was dried in a desiccator with calcium chloride as the drying agent. The indicator compound was a light brown colored solid which blackened at 240-245° C but did not melt below 305° C.

The indicator compound was colorless in acid and yellow in basic solution. The pH range was found to be 6.4 - 8.2 .

Theoretical chlorine for $C_{16}H_{10}O_4Cl_2$ 21.03 per cent.

Chlorine found 19.98 per cent.

Theoretical molecular weight for p-chlorophenolmalein 337.15 .

Molecular weight found 332.06 .

<u>o-chlorophenolmalein-</u>

A mixture of fifteen grams of maleic anhydride, forty grams of o-chlorophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 145-155° C for twelve hours with frequent stirring. The reaction mixture was placed in about six hundred milliliters of distilled water and steam distilled for one hour to remove any unreacted phenol.

The liquid which remained in the flask was cooled to room temperature and filtered. The volume of the liquid was reduced by rapid evaporation to concentrate the indicator, then cooled to allow the solid to crystallize out of the liquid. The solid was removed by filtration and purified by recrystallization from alcohol-carbon tetrachloride solution according to the procedure reported by Webster and Kamstra (12).

The product, a brown colored solid was dissolved in acetone to make a five per cent solution which was allowed to run through a chromatographic column using Merck alumina as the adsorbent. The column developed several layers each representing a distinct compound. After extruding the column, it was found that the dark brown colored layer at the lower end of the column was the indicator compound. It was eluted from the alumina with a dilute ammonium hydroxide solution. The alkaline solution of the indicator was made slightly acid with dilute hydrochloric acid. This solution was evaporated to dryness on the steam bath. The solid residue contained some ammonium chloride from the neutralization which was separated from the indicator by mixing with ether. The ammonium chloride which did not dissolve in the ether was separated from the solution by filtration. The ether solution was evaporated on the steam bath leaving the solid indicator.

The compound was dried in a desiccator with calcium chloride as the drying agent. The indicator compound was a violet colored solid which blackened at 210-215° C but did not melt below 305° C.

The indicator compound was yellow in acid and a yellow orange in basic solution. The pH range was found to be 4.5 - 6.5 .

Theoretical chlorine for $C_{16}H_{10}O_4Cl_2$ 21.03 per cent.

Chlorine found 20.68 per cent.

Theoretical molecular weight for o-chlorophenolmalein 337.15 .

Molecular weight found 336.02 .

m-chlorophenolmalein-

A mixture of fifteen grams of maleic anhydride, forty grams of m-chlorophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 160-170° C for twelve hours with frequent stirring. The reaction mixture was placed in about six hundred milliliters of distilled water and steam distilled until all of the unreacted phenol was removed.

The liquid which remained in the flask was cooled to room temperature, filtered and the product extracted with ether. The ether was evaporated on the steam bath.

In order to purify the product, this solid was dissolved in acetone and allowed to run through a chromatographic column with Merck alumina as the adsorbent. After extruding the column, it was thought that the orange colored layer at the lower end of the column was the product desired. It was eluted from the alumina with a ten per cent solution of alcohol-water and filtered. The indicator type compound remained after the solvent was evaporated.

The product was dried in a desiccator with calcium chloride as the drying agent. The compound was a light orange colored solid which blackened at 270-275° C but did not melt below 305° C.

Although its general structure is very similar to that of the others prepared, this compound was yellow in both acid and base and therefore is not an indicator.

Theoretical chlorine for $C_{16}H_{10}O_4Cl_2$ 21.03 per cent.

Chlorine found 14.75 per cent.

Theoretical molecular weight for m-chlorophenolmalein 337.15 .

Molecular weight found 272.78 .

o-bromophenolmalein-

A mixture of fifteen grams of maleic anhydride, fifty three grams of o-bromophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 130-140° C for twelve hours with frequent stirring. The reaction mixture was placed in about six hundred milliliters of distilled water and steam distilled for one hour to remove any unreacted phenol.

The liquid which remained in the flask was cooled to room temperature, filtered and the product extracted with ether. The ether extract was evaporated on the steam bath and the resulting solid was recrystallized from an alcohol-carbon tetrachloride solution according to the procedure of Webster and Kamstra (12).

To assure maximum purity, this solid was dissolved in acetone to make up a five per cent solution which was allowed to run through a chromatographic column with Merck alumina as the adsorbent. After extruding the column, it was found that the bright red colored layer at the lower end of the column was the indicator compound. It was eluted from the alumina with a ten per cent alcohol-water solution. The indicator compound remained after the solvent was evaporated. The product was dried in a desiccator with calcium chloride as the drying agent. The indicator compound was a bright red colored solid which blackened at 70-75° C and melted at 89-90° C. The indicator compound was yellow in acid and red in basic solution with a pH range of 5.1-6.8.

Theoretical bromine for $C_{16}H_{10}O_4Br_2$ 37.51 per cent.

Bromine found 36.81 per cent.

Theoretical molecular weight for o-bromophenolmalein 426.07 .

Molecular weight found 424.28 .

o-iodophenolmalein-

A mixture of fifteen grams of maleic anhydride, seventy grams of o-iodophenol and twenty grams of anhydrous stannic chloride was heated to a temperature of 110-120° C for twelve hours with frequent stirring. The reaction mixture was placed in six hundred milliliters of distilled water and heated to 70-90° C for about fifteen minutes.

The liquid which remained in the flask was cooled to room temperature, filtered and the product extracted with ether. The ether was evaporated on the steam bath and the resulting solid was dissolved in acetone to make a five per cent solution and allowed to run through a chromatographic column with Merck alumina as the adsorbent. After extruding the column, it was found that the bright red layer at the lower end of the column was the indicator compound. It was eluted from the alumina with a ten per cent alcohol-water solution. The pure indicator compound remained after the solvent was evaporated. The o-iodophenolmalein was a red colored solid which blackened at 85-90° C and melted at 96-97° C. The indicator compound was yellow in acid and red in basic solution with a pH range of 5.3 - 7.3 .

Theoretical iodine for $C_{16}H_{10}O_4I_2$ 48.81 per cent.

Iodine found 49.68 per cent.

Theoretical molecular weight for o-iodophenolmalein 520.08.

Molecular weight found 528.32 .

Determination of the Indicator Range-

Two tenths gram of each indicator was dissolved in one hundred milliliters of distilled water and the visible range was determined using the Beckman pH meter. The solution was made acid with dilute hydrochloric acid, then dilute sodium hydroxide was added slowly while the pH was taken from the Beckman pH meter. The range was checked by adding dilute hydrochloric acid to the now basic solution.

Kolthoff, Laitinen and others (13) believe that indicators behave like weak acids or weak bases, the dissociated and undissociated forms of which have different color and constitution. If the undissociated form of the indicator has acid properties, and is denoted by HI, its dissociation is represented by the same equation as that of all weak acids:

$$\underset{\text{Acid form has acid color}}{HI} \rightleftharpoons H^+ + \underset{\text{Basic form has Alkaline color}}{I^-}$$

Quantitatively the equilibrium is governed by:

$$\frac{[H^+]\ [I^-]}{[HI]} = K_I$$

where K_I is the ionization constant of the indicator. The color of the indicator in a solution is determined by the ratio of $[I^-]$ to $[HI]$.

Both forms of the indicator are present in the solution at any hydrogen-ion concentration. The phrase "visual pH range" or "useful visual range" comes from the fact that the eye has a limited sensitivity to color. Only a certain amount of one form can be detected in the presence of the other; so the visible color change of the indicator falls within certain limits of the hydrogen-ion concentration.

If the two limits of the perceptible change are expressed in pH, the region between the two limiting values in the interval of change is usually designated as color-change interval. The distinct change from the acid to the alkaline color takes place between the two limiting values, which can be determined experimentally. It should be realized that figures on the color-change interval reported in the literature have only an approximate character; from the above it is evident that the two limiting values depend more or less upon the subjective judgment of the observer. The magnitude of the interval is not the same for all indicators because the sensitivity with which the eye can perceive a small portion of the acid form in the presence of the alkaline form or a small fraction of the alkaline form in the presence of an excess of the acid form will be different for various indicators. For indicators which change from a colorless to a colored form (one color indicators) the color-change interval is greatly dependent upon the concentration of the indicator.

It is proposed that about ten per cent of the alkaline form of the indicator in the presence of the acid form can be detected as indicated by the following:

$$\frac{[I^-]}{[HI]} = \frac{1}{10} = \frac{K_I}{[H^+]} \qquad [H^+] = 10\ K_I \qquad pH = pK_I - 1$$

The eye observes the indicator to be completely in the alkaline form when in reality ninety per cent of the indicator is in the alkaline form as indicated in the following:

$$\frac{[I^-]}{[HI]} = 10 = \frac{K_I}{[H^+]} \qquad pH = pK_I + 1$$

This theory indicates that most indicators will have a pH range of two. A truer picture of the change of alkaline to acid form or vice versa for the indicators are indicated on graphs 1, 2, 3 and 4.

TABLE I

Titration of p-chlorophenolmalein with 0.094 N NaOH

NaOH ml	pH
	2.2
2	2.28
4	2.38
6	2.49
8	2.61
10	2.75
12	2.91
14	3.08
16	3.25
18	3.43
20	3.63
22	3.82
24	4.03
26	4.27
27	4.40
28	4.55
29	4.79
30	5.07
30.5	5.27
31	5.64
31.5	6.43
32	8.20
32.5	9.13
33	9.60
33.5	9.91
34	10.20
34.5	10.40
35	10.53
36	10.70
37	10.82
38	10.91
39	11.00
40	11.07
42	11.15
44	11.22
46	11.27
48	11.32
50	11.36

TABLE II

Titration of o-chlorophenolmalein with 0.094 N NaOH

NaOH ml	pH
	3.10
2	3.25
4	3.37
6	3.47
8	3.59
10	3.71
12	3.87
14	4.07
15	4.16
16	4.30
17	4.44
18	4.60
19	4.73
20	4.91
21	5.10
22	5.25
23	5.40
24	5.88
25	6.20
26	6.39
27	6.54
28	6.68
29	6.79
30	6.85
31	6.93
32	7.00
33	7.04
34	7.10
35	7.14
36	7.19
37	7.23
38	7.28
39	7.32
41	7.39
43	7.41
45	7.43
47	7.47
49	7.51
51	7.55
53	7.60

TABLE III

Titration of m-chlorophenolmalein with 0.094 N NaOH

NaOH ml	pH
	2.9
2	2.94
4	2.99
6	3.02
8	3.06
10	3.11
12	3.15
14	3.20
16	3.23
18	3.27
20	3.31
22	3.35
24	3.38
26	3.41
28	3.45
30	3.49
32	3.52
34	3.55
36	3.59
38	3.62
40	3.65
42	3.68
44	3.72
46	3.75
48	3.79
50	3.82

TABLE IV

Titration of p-bromophenolmalein with 0.094 N NaOH

NaOH ml	pH
	1.83
2	1.86
4	1.90
6	1.94
8	1.99
10	2.05
12	2.12
14	2.23
16	2.34
18	2.46
20	2.53
21	2.65
22	2.70
23	2.98
24	3.66
24.5	5.10
25	6.70
25.5	7.50
26	8.00
26.5	8.80
27	9.40
27.5	9.80
28.	10.10
28.5	10.27
29	10.40
30	10.55
31	10.68
32	10.78
33	10.85
34	10.90
35	10.95
37	11.02
39	11.08
41	11.15
43	11.20
45	11.23

TABLE V

Titration of o-bromophenolmalein with 0.094 N NaOH

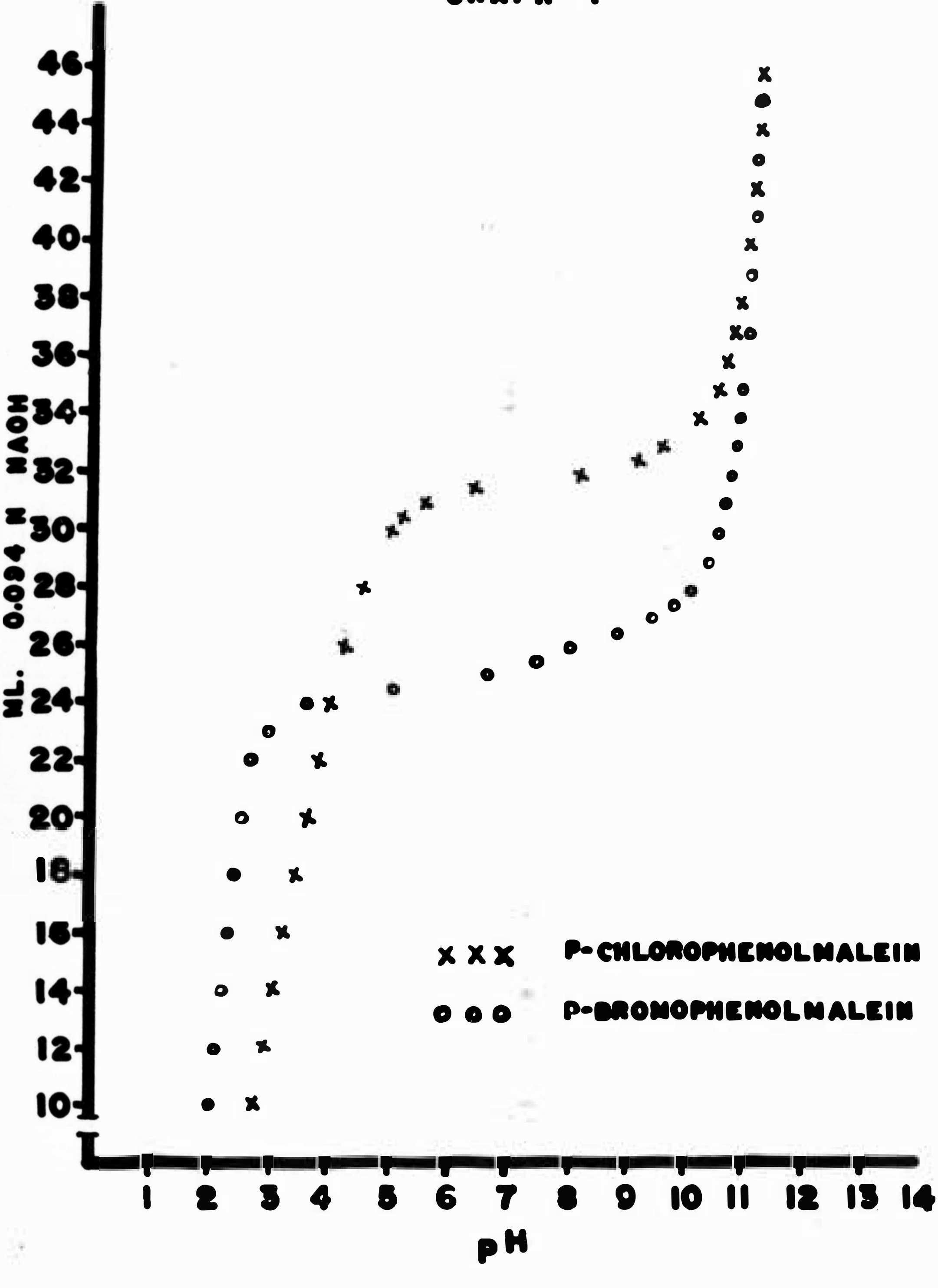
NaOH ml	pH
	2.5
2	2.54
4	2.60
6	2.72
8	2.86
10	3.02
12	3.19
14	3.38
16	3.56
18	3.75
20	3.98
22	4.20
24	4.43
26	4.75
27	4.98
27.5	5.12
28	5.32
28.5	5.55
29	5.84
29.5	6.17
30	6.41
30.5	6.63
31	6.80
31.5	6.98
32	7.12
32.5	7.27
33	7.40
33.5	7.52
34	7.65
35	7.85
36	8.05
37	8.21
38	8.40
39	8.53
40	8.65
42	8.94
44	9.23
46	9.60
48	10.02
50	10.40
52	10.68
54	10.88
56	11.00
58	11.1
60	11.17

TABLE VI

Titration of o-iodophenolmalein with 0.094 N NaOH

NaOH ml	pH
	2.50
2	2.60
4	2.76
6	2.89
8	3.06
10	3.21
12	3.38
14	3.52
15	3.60
16	3.69
17	3.78
18	3.86
19	3.94
20	4.02
21	4.11
22	4.19
23	4.28
24	4.36
25	4.45
26	4.55
27	4.67
28	4.79
29	4.94
30	5.15
30.5	5.30
31	5.50
31.5	5.83
32	6.87
32.5	9.14
33	9.88
33.5	10.49
34	10.74
34.5	10.93
35	11.08
36	11.26
37	11.37
38	11.47
39	11.55
40	11.60
42	11.70
44	11.78
46	11.83
48	11.89
50	11.93

GRAPH 1


ML. 0.094 N NAOH
46
44
42
40
38
36
34
32
30
28
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22
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18
16
14
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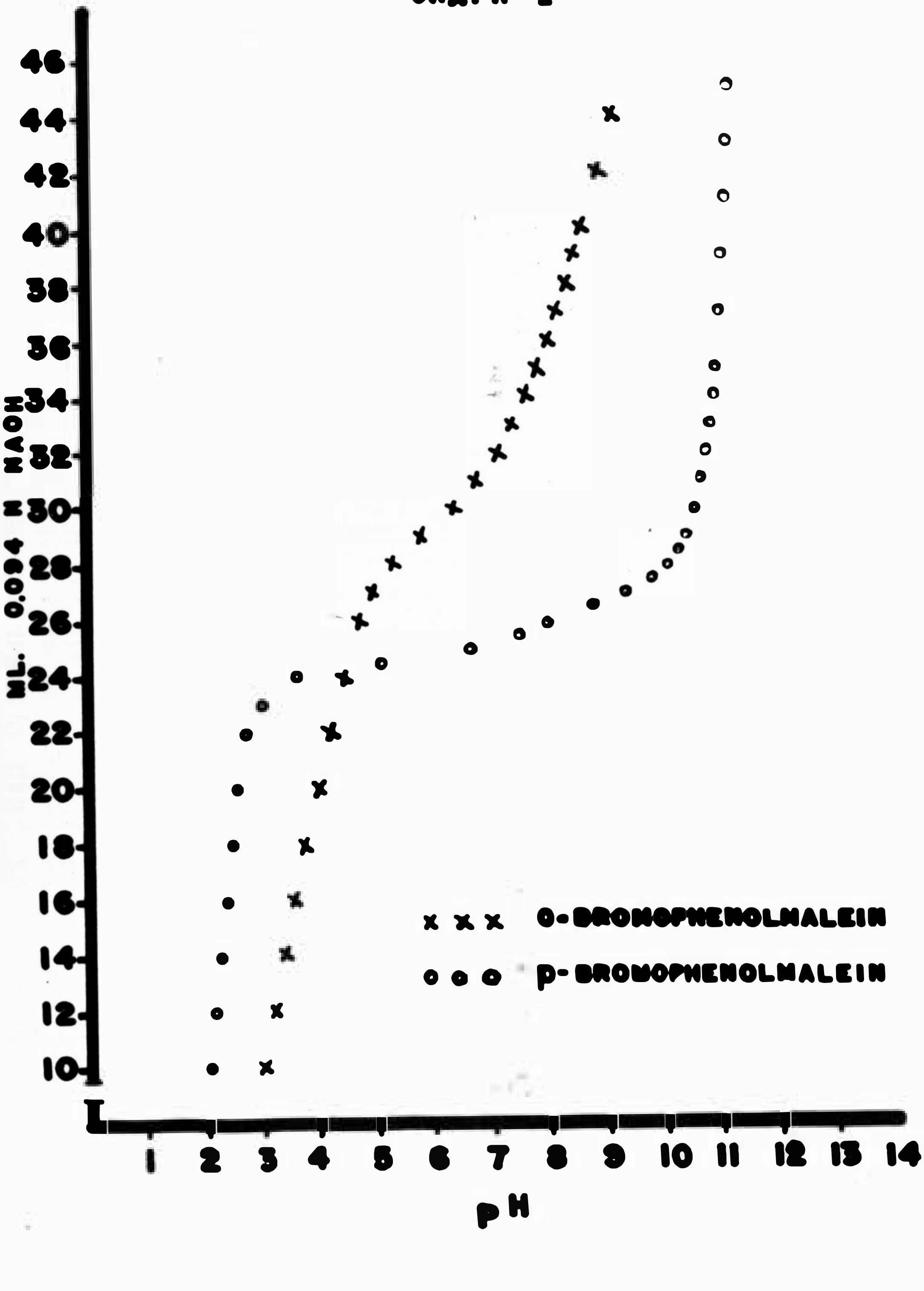
14
pH
X X X P-CHLOROPHENOLMALEIN
O O O P-BROMOPHENOLMALEIN

GRAPH 2


ML. 0.094 N NAOH
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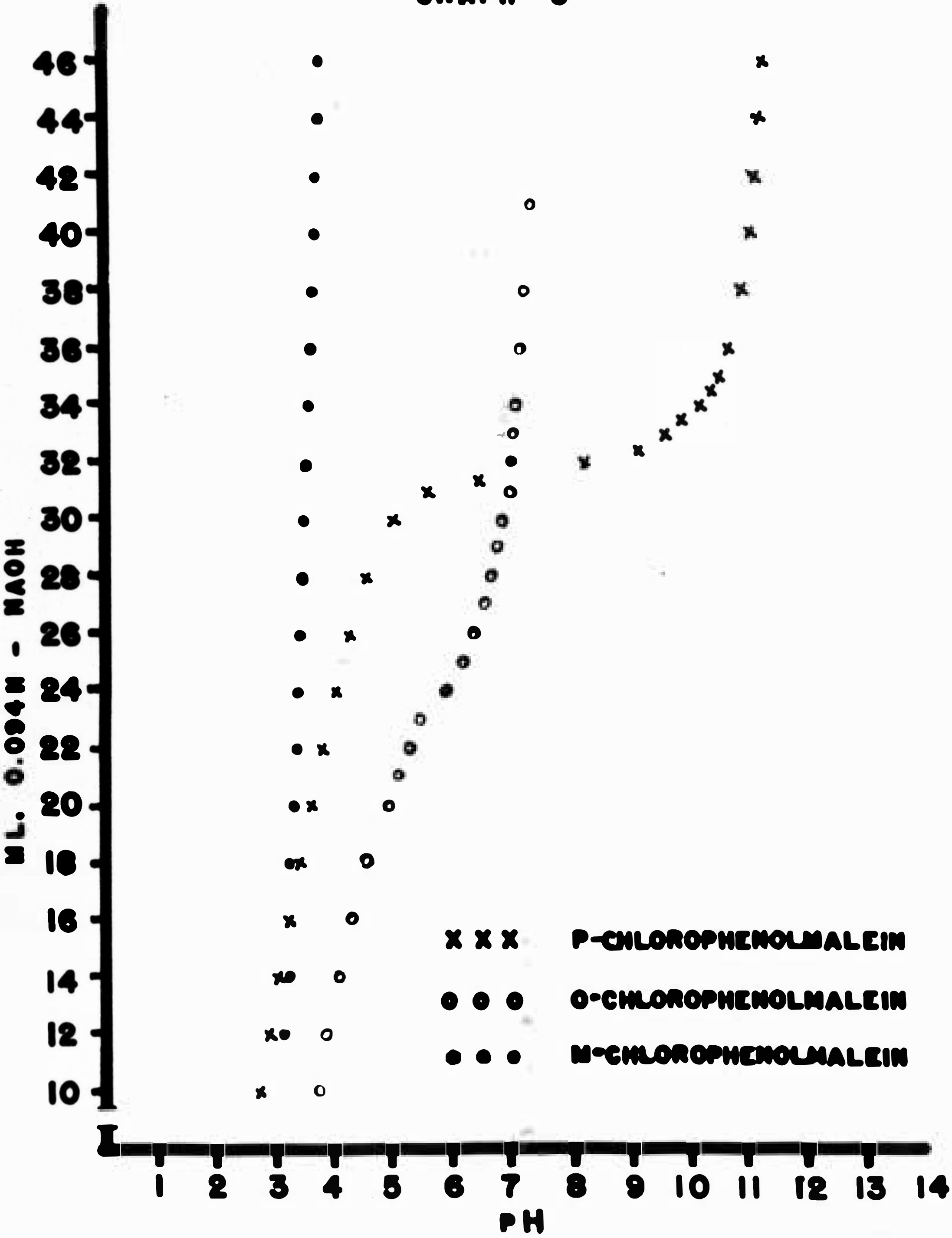
pH
x x x O-BROMOPHENOLMALEIN
o o o P-BROMOPHENOLMALEIN

GRAPH 3


ML. 0.094N - NAOH
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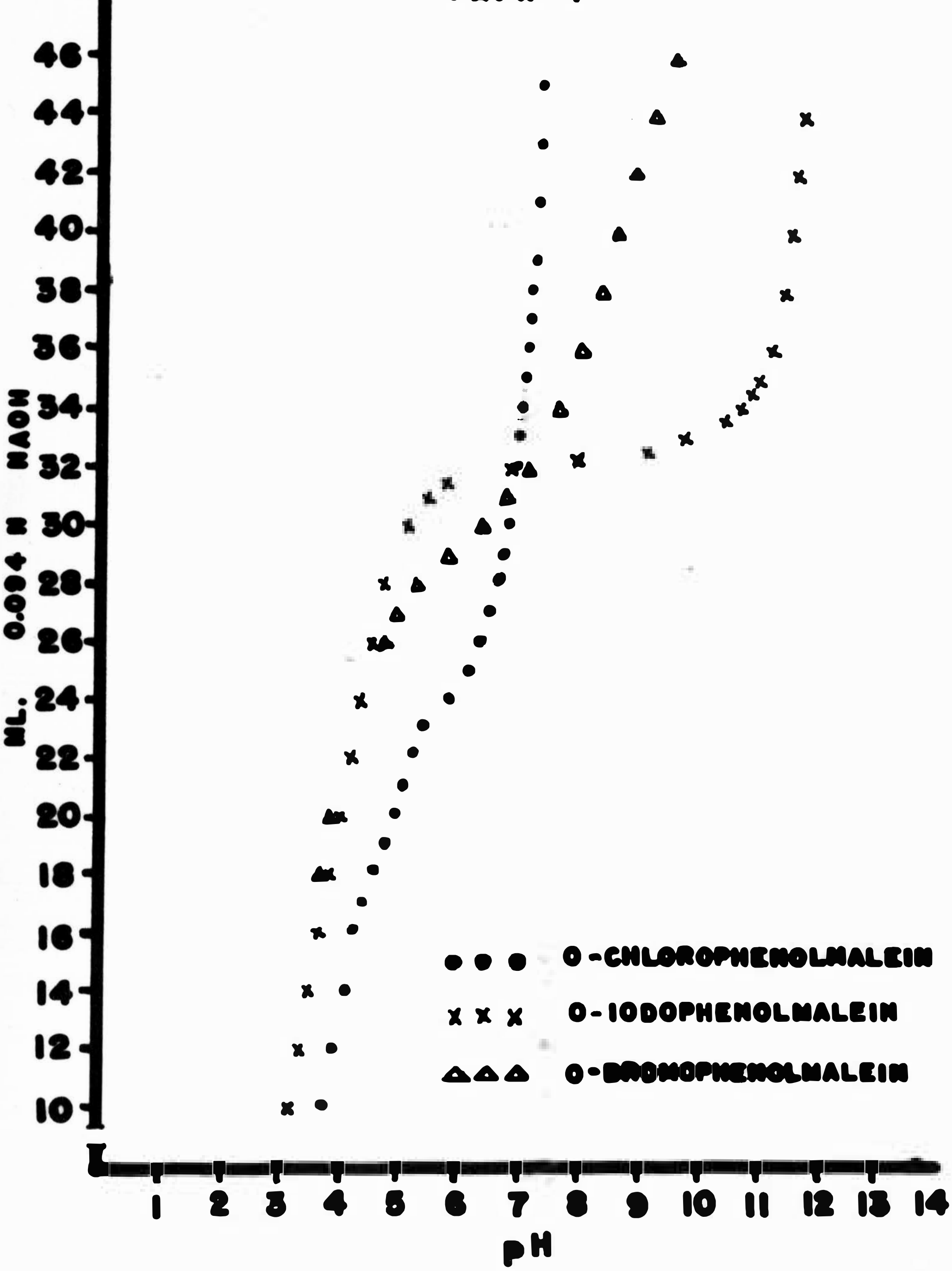
PH
x x x P-CHLOROPHENOLMALEIN
o o o O-CHLOROPHENOLMALEIN
● ● ● M-CHLOROPHENOLMALEIN

GRAPH 4


ML. 0.094 N NAOH
46
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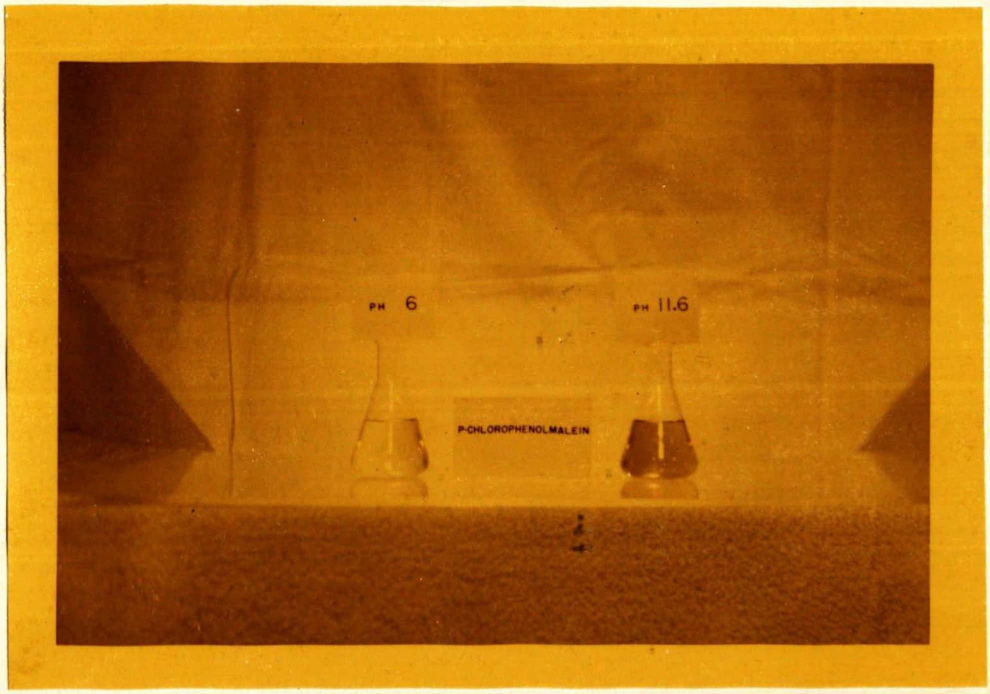
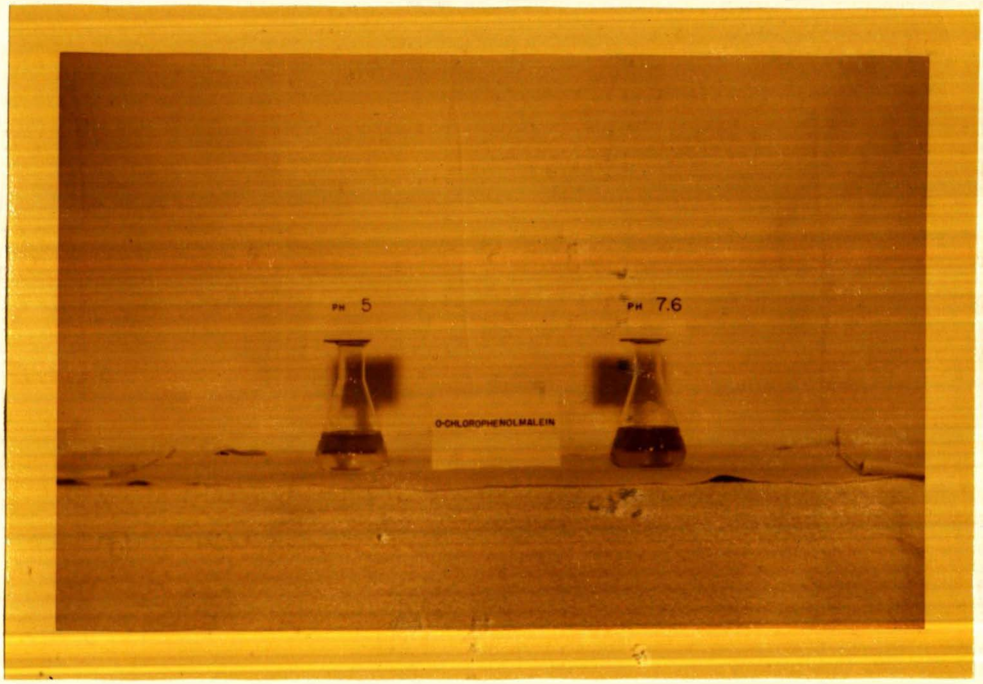
9
10
11
12
13
14
pH
● ● ● O-CHLOROPHENOLMALEIN
x x x O-IODOPHENOLMALEIN
△△△ O-BROMOPHENOLMALEIN

Plate I



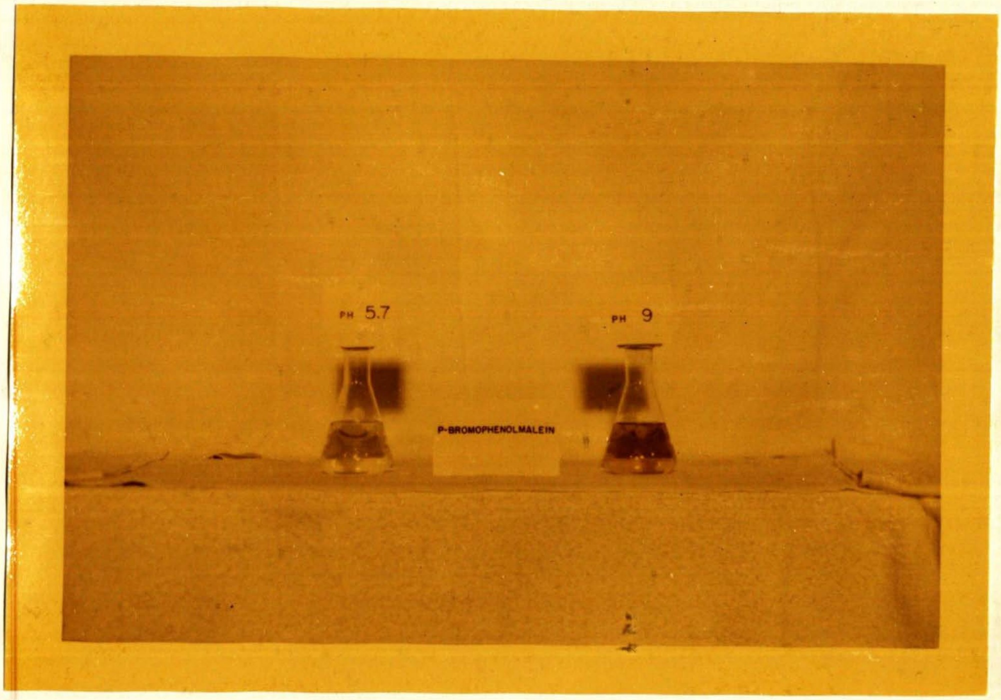
p-chlorophenolmalein

Plate II



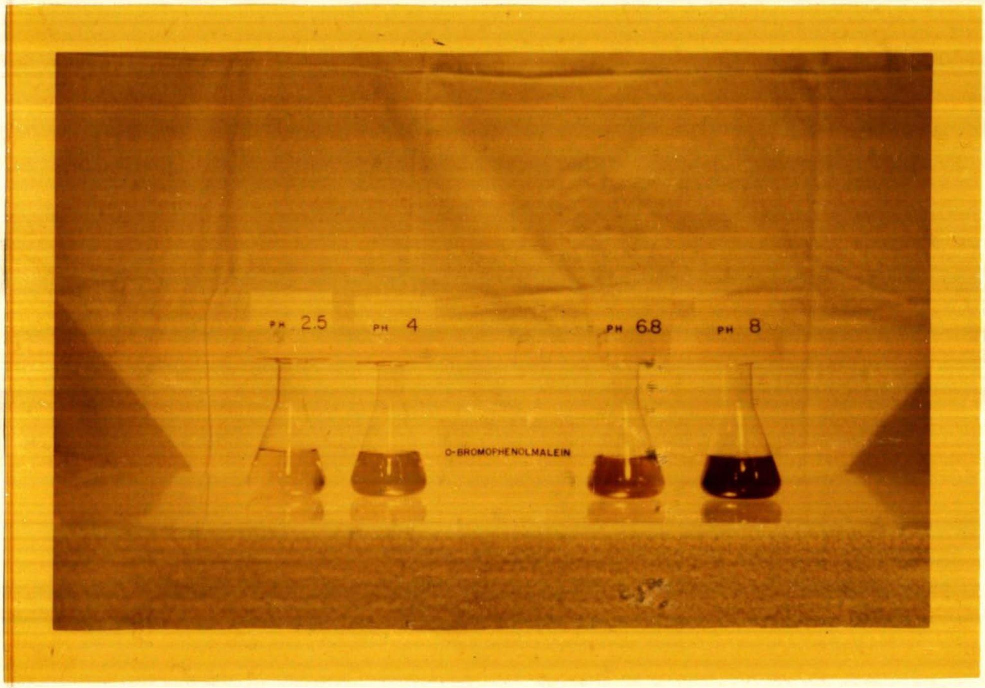
o-chlorophenolmalein

PLATE III



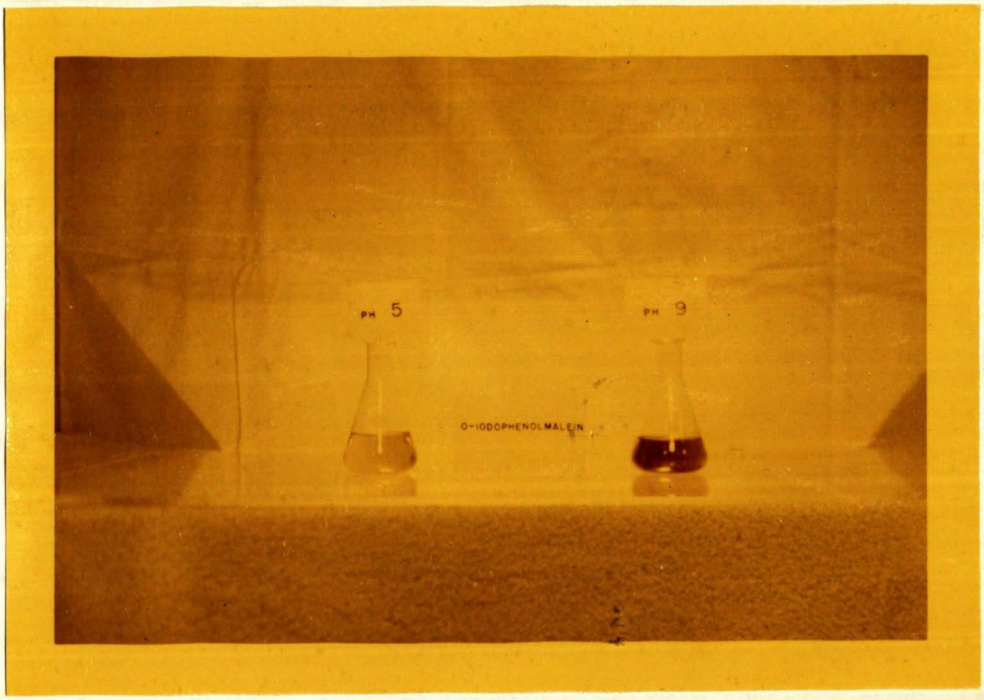
p-bromophenolmalein

PLATE IV



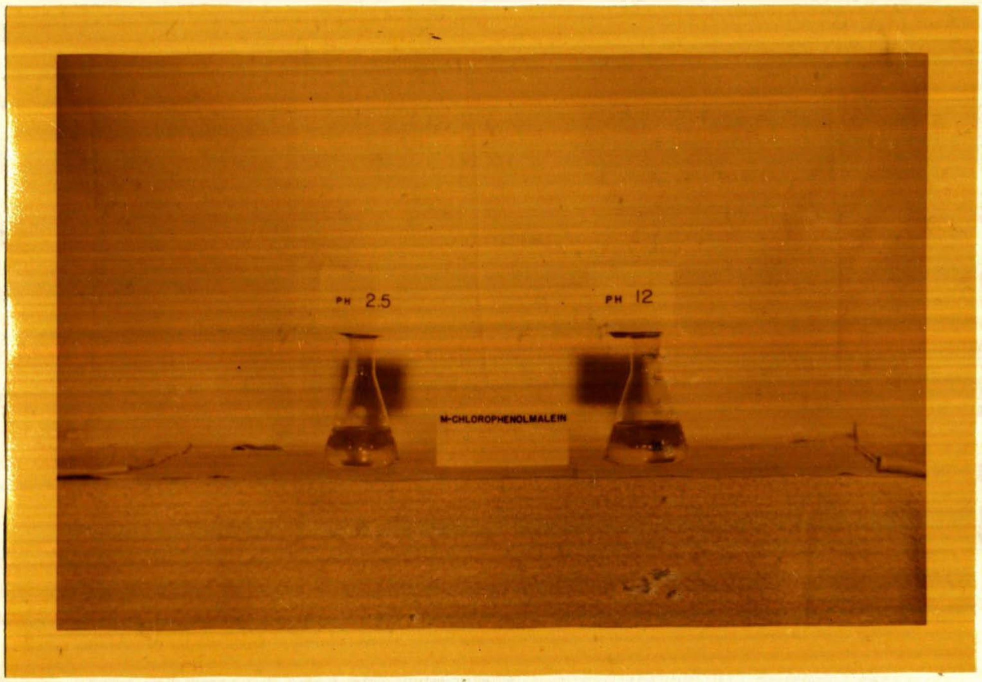
o-bromophenolmalein

PLATE V



o-iodophenolmalein

PLATE VI



m-chlorophenolmalein

Analysis

Determination of Halogen in the compounds-

The Parr Bomb procedure (16) was used to determine the amount of halogen in the indicator compounds.

A sample (approx. 0.1 g.) of indicator was fused with fifteen grams of sodium peroxide, 0.3 gram of potassium nitrate and 0.1 gram of sucrose. This fusion converted organic halogen to inorganic ionizable halogen which was then precipitated with silver nitrate and the precipitate dried and weighed.

The fusion mixture was placed in the cup of the bomb and a thin sprinkling of sucrose was added to the top to insure a fusion. The cap was screwed on the bomb tightly and the bomb was then placed in the ignition apparatus. An electromotive force of eight volts applied for fifteen seconds was used for ignition. After igniting the charge, the bomb was cooled to room temperature and opened. The melt was then dissolved in approximately one hundred milliliters of warm distilled water.

The alkaline solution was made neutral by adding dilute (1:1) nitric acid slowly with constant stirring. This solution was filtered and washed thoroughly with warm distilled water. A slight excess of 0.1 N silver nitrate was added very slowly with constant stirring.

In the determination of bromine and iodine great care was taken to prevent the loss of free iodine or bromine, which may form in the acidified solution. Ten milliliters of a four per cent solution of hydrazine sulfate was added to the boiled alkaline solution, heating below boiling until effervescence ceases. The solution was cautiously acidified and more hydrazine sulfate added at the neutral point if free iodine or bromine appears. The acidified solution was then filtered and an excess of silver nitrate added. The precipitate formed was filtered using a sintered glass filter, washed with three hundred milliliters of distilled water, dried at 140° C for one hour, cooled and weighed.

The percent halogen was calculated using the following general formula-

$$\text{per cent halogen} = \frac{\text{Wt. of AgX} \times \text{At. Wt. of X} \times 100}{\text{Wt. of sample (g.)} \times \text{M.W. of AgX}}$$

Results are found in Tables VII, VIII and IX.

Determination of Molecular Weight-

A method originally proposed by Rast and modified by Shriner and Fuson (14) and Kamm (15) was used to determine the molecular weight. This was a method making use of the molal freezing point lowering of camphor.

The cryoscopic method is based upon the accurate determination of the depression of the freezing point of a known solvent following the introduction of a known weight of solute.

A suitable solvent was picked, depending on the nature of the compound whose molecular weight was to be determined. In this case camphor was used because of its high constant value (c). The melting point of pure camphor was determined by placing a definite amount in a test tube fitted with a thermometer and a stirrer. The test tube was placed in a bath of hot concentrated sulfuric acid, the temperature of which was held fairly constant a few degrees above the expected melting point.

In order to determine the value of (c), a weighed amount of a known, phenolphthalein, and a weighed amount of camphor were placed in a twenty centimeter test tube fitted with a thermometer. Five parts of phenolphthalein to one hundred parts of camphor by weight were used. The test tube was then placed in the constant temperature bath and the mixture was melted again and this time an accurate determination of the melting point was recorded. This procedure was repeated using ten parts of phenolphthalein to one hundred parts of camphor by weight.

With the values obtained, the value for (c) was determined. This procedure was followed for each indicator with camphor. The melting points were checked at the same two concentrations of solute to solvent as above. With the data obtained, and using the formula,

$$M = \frac{c \times p}{\Delta}$$

where c = constant for the particular solvent used.
p = the number of grams of the unknown per one hundred grams of the solvent.
Δ = the depression of the freezing point.
M = molecular weight.

the molecular weight of the indicator was calculated.

Discussion of Results

Webster and Kamstra (12) proposed the condensation of maleic anhydride with p-bromophenol to give p-bromophenolmalein as follows:

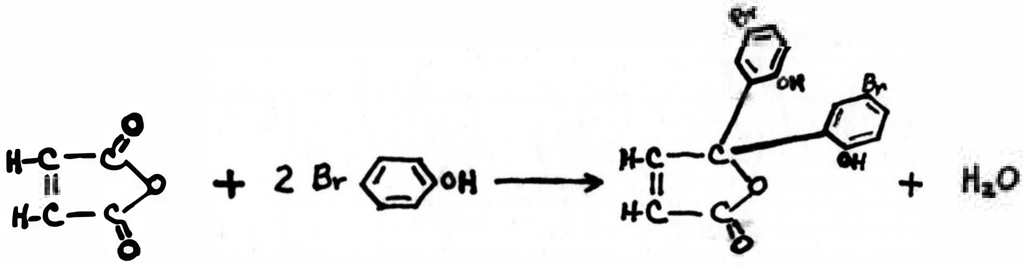


TABLE VII

MALEIN	COLOR CHANGE		PH RANGE	M.P. -°C.	MOLECULAR WT.		% HALOGEN	
	ACID	BASE			THEORET	EXP.	THEORET	EXP.
P-CHLORO PHENOL	COLORLES	YELLOW	6.4 8.2	BLACKENS 240-245 ABOVE-305	337.164	332.06	21.03	19.98
M-CHLORO PHENOL	YELLOW	YELLOW	NONE	BLACKENS 270-275 ABOVE-305	337.164	272.78	21.03	14.75
O-CHLORO PHENOL	YELLOW	YELLOW ORANGE	4.5 6.5	BLACKENS 210-215 ABOVE-305	337.164	336.02	21.03	20.68
P-BROMO PHENOL	COLORLES	RED	5.3 7.2	BLACKENS 195-200 ABOVE 305	426.094	418.00	37.51	36.34
O-BROMO PHENOL	YELLOW	RED	5.1 6.8	BLACKENS 70-75 89-90	426.094	424.28	37.51	36.81
O-IODO PHENOL	YELLOW	RED	5.3 7.3	BLACKENS 85-90 96-97	520.084	528.32	48.81	49.68

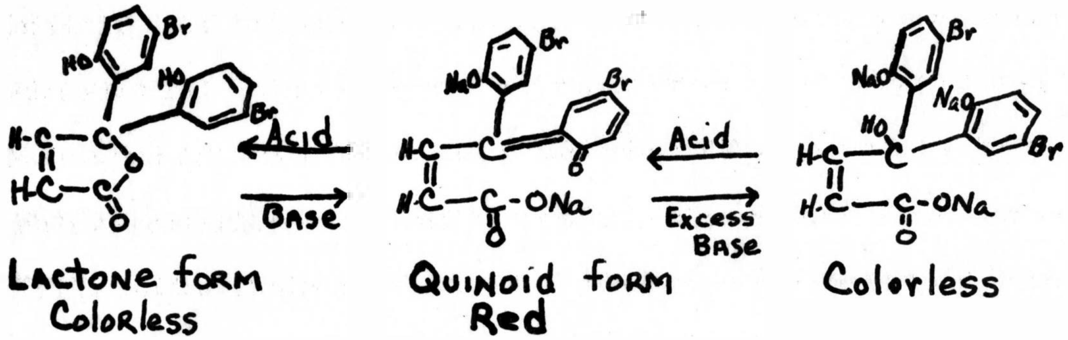
TABLE VIII
DETERMINATION OF HALOGEN

MALEIN	SAMPLE WT. GRAMS		Ag X WT. GRAMS		HALOGEN WT. GRAMS		% HALOGEN		THEOR. HALOGEN
	TRIAL 1	TRIAL 2	TRIAL 1	TRIAL 2	TRIAL·1	TRIAL 2	TRIAL·1	TRIAL 2	
P·CHLORO PHENOL	0.1087	0.1164	0.0868	0.0924	0.0215	0.0228	20.21	19.64	21.03
M·CHLORO PHENOL	0.1059	0.1243	0.0663	0.0705	0.0164	0.0174	15.48	14.03	21.03
O·CHLORO PHENOL	0.1107	0.1283	0.0918	0.1082	0.0227	0.0268	20.51	20.88	21.03
P·BROMO PHENOL	0.1092	0.1132	0.0922	0.0978	0.0392	0.0416	35.92	36.76	37.51
O·BROMO PHENOL	0.1225	0.1044	0.1072	0.0893	0.0456	0.0380	37.23	36.39	37.51
O·IODO PHENOL	0.1028	0.0986	0.0956	0.0896	0.0517	0.0484	50.26	49.11	48.81

TABLE IX

MOLECULAR WEIGHT DETERMINATION

MALEIN	SAMPLE WT. GRAMS		CAMPHOR WT. GRAMS		DEPRESSION OF M.P.		MOL. WT.		M. W. THEORE.
	TRIAL 1	TRIAL 2	TRIAL 1	TRIAL 2	TRIAL 1	TRIAL 2	TRIAL 1	TRIAL 2	
P-CHLORO PHENOL	0.100	0.100	2.00	1.00	6.4	12.5	328.12	336.00	337.16
M-CHLORO PHENOL	0.100	0.100	2.00	1.00	7.8	15.2	269.23	276.32	337.16
O-CHLORO PHENOL	0.100	0.100	2.00	1.00	6.2	12.6	338.71	333.34	337.16
P-BROMO PHENOL	0.100	0.100	2.00	1.00	5.1	9.9	411.76	424.24	426.08
O-BROMO PHENOL	0.100	0.100	2.00	1.00	5.0	9.8	420.00	428.57	426.08
O-IODO PHENOL	0.050	0.100	1.00	1.00	4.0	7.9	525.00	531.64	520.08



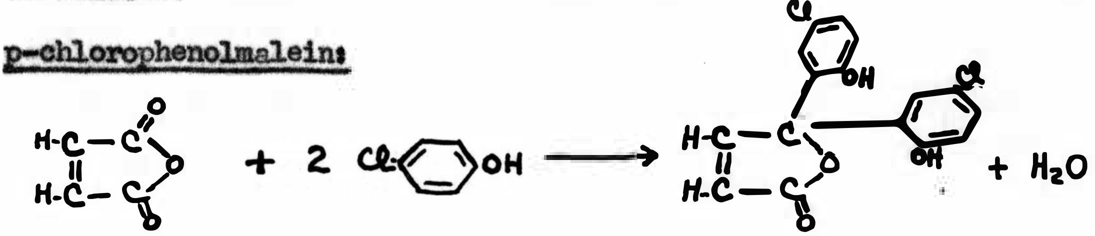
It seemed very likely that o-bromophenol, o-iodophenol, p-chlorophenol, o-chlorophenol and m-chlorophenol would react similarly with maleic anhydride.

With due consideration of experimental error, the analysis for halogen and molecular weight gave evidence in favor of such a structure except in the case of m-chlorophenol.

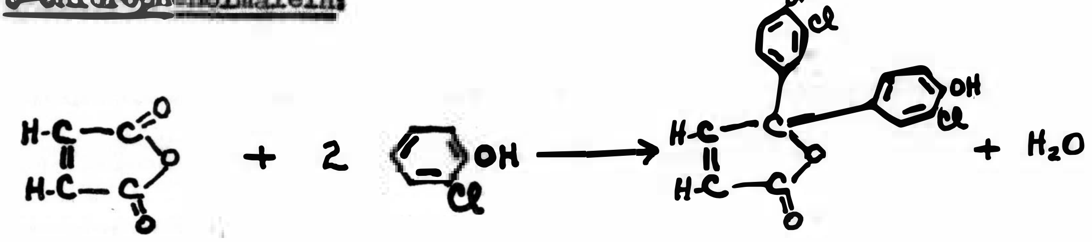
The results of the analysis for chlorine from this compound differed too widely from the theoretical value for m-chlorophenolmalein to give conclusive support for its preparation. It must be stated then that either m-chlorophenolmalein was not obtained from the reaction or it was too impure to give correct analytical results.

Equations representing the reactions for the preparation should be as follows:

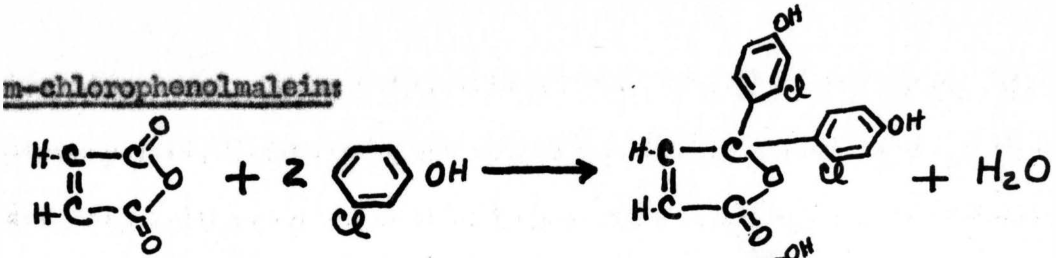
p-chlorophenolmalein:



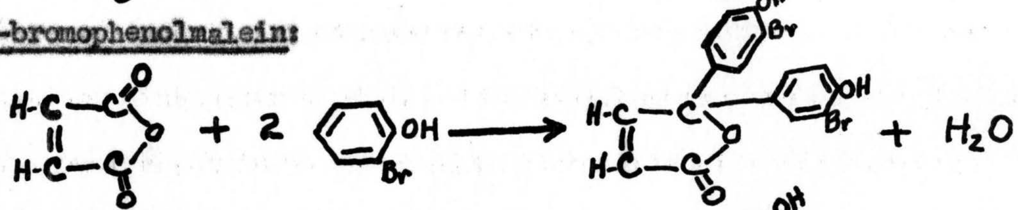
o-chlorophenolmalein:



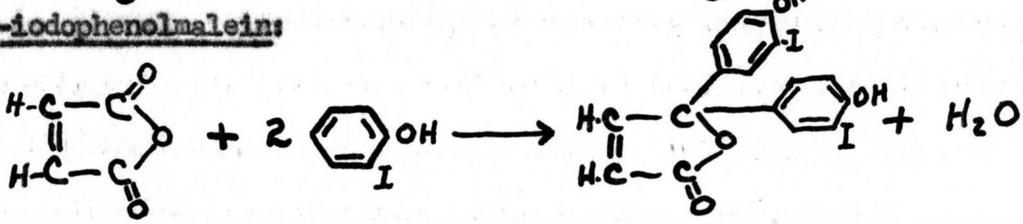
m-chlorophenolmalein:



o-bromophenolmalein:



o-iodophenolmalein:



The colorless form in acid medium was observed in the cases of p-chlorophenolmalein and p-bromophenolmalein. The others exhibited varying degrees of yellow in acid solution. P-bromophenolmalein and o-iodophenolmalein exhibited a tendency to fade in the higher alkaline range of pH much the same as phenolphthalein does.

The titration curves of the indicators, graphs 1, 2, 3 and 4 show some interesting relationships between the ortho, meta and para position of the halogen in the phenolmalein structure and the shape of the curve. Para derivatives have the sharpest curve and sharpest end point, ortho derivatives have a more general curve, not so sharp an end point and the meta derivative a straight line with no color change in acid-base titration. Of the ortho derivatives, the iodo gave the sharpest curve followed by the bromo and chloro derivatives in that order. Iodo and bromo derivatives produced brighter colors than chloro in acid and basic solution.

The color shades through which the indicators passed in going through the visible pH range are shown by Plates I, II, III, IV, V and VI.

Suggestions for Further Work

The condensation products using the p-iodophenol, m-iodophenol and m-iodophenol with maleic anhydride would be of interest to determine how they fit into the picture of the halogenated phenolmaleins.

It would be of interest to determine how large an anhydride ring will react to give the phenol-anhydride condensation.

It would also be of interest to determine how large a phenol type ring will react to give the phenol-anhydride condensation.

The condensation of ortho, meta and para nitrophenol, methyl phenol (cresol) and aminophenol should give condensation products with possible indicator properties. It would be of interest to see how they would compare in physical properties to those of the indicators reported in this thesis.

Special consideration should be given to the problem of determining the optimum conditions of time, temperature and catalyst in these condensation reactions.

Further work should be done with m-chlorophenol to obtain a pure product and to determine its properties.

Summary

Four new indicator-type compounds, p-chlorophenolmalein, o-chlorophenolmalein, o-bromophenolmalein and o-iodophenolmalein have been prepared, purified and analyzed and the molecular weight determined.

P-bromophenolmalein was also prepared but some of its properties were found to differ from those reported by Webster and Kamstra (12).

The preparation of m-chlorophenolmalein was attempted but the results of the analysis indicated that the product was not sufficiently pure for a study of its properties.

A study has been made of the pH range, color changes and titration curves of the six indicator type compounds mentioned above.

All the ortho and para derivatives which were prepared have shown indicator properties. The compound obtained from m-chlorophenol showed no color change in acid-base titrations.

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