THE RELATIVE REACTIVITY OF ACETIC ESTERS WITH ANILINE

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Preface.

The purpose of this thesis was to ascertain the relative reactivity between aniline and the esters of acetic acid. It was proposed to determine the reactivity of methyl, ethyl, butyl and phenyl esters of acetic acid with aniline.

The general reaction is represented by the following equation: CH_3COOR plus $C_6H_5NH_2$ gives $C_6H_5NH-COCH_3$ plus XOH in which R is the radical particular to the ester. The reaction gives acetanilide in every case and the alcohol corresponding to the ester used.

The only information found was that of Leo Vignon & Evieux who did work using aniline in reaction with acetic acid and benzoic acid in benzene; This information was valuable only indirectly. And much credit must be given to Dr. R. Q. Brewster and Dr. H. F. Dains for the outlining of the work and under whose direction this thesis was worked out.

The plan outlined was that of interacting theoretical amounts, of aniline and the ester according to the equation above, at a certain temperature for different lengths of time and then also for a certain length of time but at different temperatures.

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PREPARATION AND PURIFICATION OF THE ESTERS AND ANILINE.

The first esters prepared were butyl acetate and phenyl acetate.

The preparation of butyl acetate was made by the usual method by the interaction of acetic acid and butyl alcohol in presence of concentrated sulfuric acid. 60 grams of acetic acid and 74 grams of butyl alcohol were mixed together in a two liter round bottom flask and then 25 grams of concentrated (specific gravity 1.84) sulfuric acid were added very slowly to prevent heating and volatilization of the butyl alcohol. The flask was placed on a sand bath and fitted with a vertical condenser; then refluxed for four hours. After which time the condenser was removed and a strong solution of sodium carbonate was added to the mixture. The layer of butyl acetate formed on top and sodium carbonate was added until this layer was no longer acid, after which time the butyl acetate was separated as completely as possible, by the use of a separatory funnel, and then dried over dehydrated sodium sulfate for four hours. The dried ester was then placed in

a small distilling flask connected with a condenser and thermometer and fractionally distilled. After several fractionations a constant boiling point of 125 degrees centigrade was obtained. The recorded boiling point is 125.1 degrees centigrade. The yield calculated on the amount of butyl alcohol used was 70 grams or 60.5%. The yield was low and can possibly be accounted for by losses due to the number of fractional distillations undergone.

The equation is as follows:

CH_3COOH plus C_4H_9OH gives $CH_3COOC_4H_9$ plus H_2O.

Preparation of Phenal Acetate.

Phenal acetate was first prepared in a similar method as used in preparing butyl acetate. 60 grams of acetic acid and 86 grams of phenol were mixed together in a two liter round bottom flask. To this 25 grams of concentrated sulfuric acid were added very slowly to prevent any unnecessary heating. Immediately upon the addition of the sulfuric acid the mixture of acetic acid and phenol turned to a deep brown color. However the mixture was refluxed for four hours using a

water condenser. After which time the mixture was allowed to cool, but no layer of the ester could be noticed. The problem was to separate the phenylacetate from the rest of the solution, which contained phenol, acetic acid and sulfuric acid if there was any reaction as theoretically supposed. An attempt was made to wash out the excess phenol with dilute sodium hydroxide and then distill over the ester, but with little success. Steam distillation was then resorted to, knowing that only the ester would distill over providing the rest of the mixture was slightly alkaline. This method gave only a 5% yield, and the reason for such a low yield was probably due to the formation of aniline hydrogen sulfate when the concentrated sulfuric acid was first added.

Finally this ester was prepared by the interaction of acetic anhydride and phenol. 102 grams of acetic anhydride and 93 grams of phenol were mixed together in a half liter flask to which was connected an upright water condenser and refluxed for two hours. After this time there was a distinct layer of the ester formed and the mixture was clear.

A strong solution of sodium carbonate was added until the solution was slightly alkaline. The mixture was then poured in a two liter flask connected to a horizontal condenser and steam distilled. The ester was washed several times with distilled water and then separated as completely as possible by the use of a separatory funnel. The washed ester was then dried over dehydrated sodium sulfate for two hours, after which it was fractionally distilled over a free flame using an air condenser until a constant boiling point of 196 degrees centigrade was obtained. The recorded boiling point is 196.7 degrees centigrade. (Van Nostrand Chemical Handbook.) The yield calculated on the weight of aniline used was 46%. Equation as follows: $CH_3CO)^2O$ plus C_6H_5OH gives $CH_3COOC_6H_5$ plus CH_3COOH.

Preparation of Methyl Acetate.

Methyl acetate was prepared by the interaction of acetic acid and methyl alcohol. A distilling flask ($\frac{1}{2}$ liter) was attached to a condenser and a receiver. The flask was provided with a cork, through which a separatory funnel and a thermometer were inserted. The former extended down into the liquid in the flask. A mixture of 50cc methyl alcohol and 50cc of

concentrated sulfuric acid were poured into the flask, which was then heated in a bath of paraffin wax to 140 degrees centigrade and kept at this temperature. A mixture of equal volumes of glacial acetic acid (50cc) and methyl alcohol, (50cc) was then added, drop by drop, from the separatory funnel at the speed at which the liquid distilled. When all the mixture had been added the distillation was stopped and the distillate which contained the ester and also acetic acid, alcohol and sulfurous acid, was shaken in a separatory funnel with a strong solution of sodium carbonate until the layer of methy acetate ceased to redden blue litmus. The lower layer was then removed as completely as possible and the layer of methyl acetate dried over calcium chloride for two hours. After which the ester was placed in a 100cc distilling flask connected to a water condenser and distilled from a water bath. The ester was fractionally distilled until a constant boiling point of 57 degrees centigrade was obtained. The recorded boiling point is 54.05 degrees centigrade.

Equation:

CH_3COOH plus CH_3OH gives CH_3COOCH_3 plus H_2O.

Purification of Ethyl Acetate.

A stock of ethyl acetate was at hand so no more was made; however it was first fractionally distilled until a boiling point of 76.8 degrees centigrade was reached. The recorded boiling point is 77.15 degrees centigrade. (Van Nostrand Chemical Annual).

Purification of Aniline.

Aniline was obtained as a dark impure commercial product. This was fractionally distilled over metallic zinc to reduce any nitrobenzene, until a constant boiling point of 183 degrees centigrade was obtained. The recorded boiling point is 184.4 degrees centigrade (Van Nostrand's Chemical Annual).

Separation of Acetanilide.

The interaction of any one of the acetates, methyl, ethyl, butyl or phenyl, with aniline will result in the formation of acetanilide and alcohol of the ester used. Consequently the amount of acetanilide formed would be a measure of the completeness of the reaction, and a method for the separation of substance from the rest of the mixture is necessary. For a trial separation one twentieth molar proportions of the

reacting substances were taken as if one-half of the original substance had reacted, giving 6 grams of butyl acetate, 5 grams of aniline, 7 grams of acetanilide, 4 grams of butyl alcohol, all of which were mixed well in a test tube and heated until a clear solution was obtained. The mixture was then washed with dilute hydrochloric acid which took out most of the aniline and butyl alcohol, and separated as completely as possible from the mixture of ester and acetanilide by the use of a separatory funnel. The mixture was next placed in a small distillation flask connected to a water condenser. The mixture was made almost neutral to prevent the decomposition of acetanilide, and the ester distilled over leaving the acetanilide in solution in the distilling flask, This solution was concentrated and the acetanilide crystallized at a temperature of zero degrees centigrade. The crystallized substance was filtered dried at 100 degrees centigrade and weighed, with a result of 4.2 grams or a 60% recovery of the acetanilide.

The small recover could be placed to several different reasons so another method and much simpler was tried. This time an 100cc round

bottom flask was fitted with a tight stopper, through which are passed two glass tubes; one leading to the bottom of the test tube, through which steam was to be passed and the other tube, which just protudes, just through the cork, leads to a water condenser. 6 grams of butyl acetate, 5 grams of aniline, 7 grams of acetanilide and 4 grams of butyl alcohol were placed in the flask and heated until the mixture was clear. Then twenty cc. of water added to the mixture and the whole steam distilled until the distillate came over clear. The residue was then cooled to the temperature of melting ice at which the acetanilide separated out immediately. The whole was filtered and the crystallized product dried at 100 centigrade and weighed. With a result of 6.95 grams of acetanilide or 99.4% recovery. This method was used with the other esters and results within 0.1% were obtained. Consequently several sets of apparatus were made up, one apparatus for each ester.

CONDITIONS OF REACTION.

The next step was to find out under what conditions the different esters would react with aniline. Butyl acetate and aniline were first tried. Reaction at atmospheric pressure was first to be ascertained; so one twentieth molar portions of butyl acetate and aniline were mixed in an eight inch hard glass test tube fitted with a condenser and refluxed over an oil bath, at 160 degrees centigrade for two hours. The mixture was then washed with alcohol into the separating apparatus and diluted with 20cc water. The whole was steam distilled until the distillate was no longer cloudy. The residue left in the flask was concentrated and cooled to the temperature of melting ice. No acetanilide separated out, showing that butyl acetate and aniline do not react under these conditions.

A second trial was made using one twentieth molar portions which are 5.8 grams butyl acetate and 4.8 grams of aniline and should give theoretically a yield of 6.7 grams of acetanilide. The mixture was placed in an eight inch test tube, fitted with an upright water condenser and refluxed over a metal bath at a temperature of 220

degrees centigrade for forty eight hours, giving a yield of 19.8%. This method proved too long so heating the mixture in a bomb tube was resorted to.

Bomb tubes were made of hard glass 2.5cm tubing. One end of the tubing was sealed off, the mixture placed in the tube and then the other end sealed off. The tubes were all made approximately the same length, had to be at least 14 inches long to prevent "blowing out" when the final seal was made. 5.8 grams of butyl acetate and 4.8 grams of aniline were placed in one of these tubes and sealed. The tube was then placed in a "bomb" furnace and heated at 220 degrees for 21 hours. The bomb furnace consists of four iron tubes about two inches in diameter and two feet long, encased in sheet iron and provided with gas heat. The bombs are slipped inside of these tubes and the heat turned on. A very steady temperature can be obtained for almost any length of time. After 21 hours of heating the mixture was cooled, bomb opened and washed into the steam distilling flask with alcohol and steam distilled until the distillate becomes clear. The tube was opened and no internal pressure or vaccus noted. The contents were distilled until the distillate

becomes clear. The residue in the flask was then concentrated and the acetanilide crystallized put at the temperature of melting ice, filtered, dried and weighed. The mixture was found to have reacted and gave a yield of 1.93 grams of acetanilide or 30%.

One twentieth molar portions of the remaining esters and aniline were then tried with the same method and the following results were obtained:

Methyl acetate and aniline - 220 degrees for 21 hours --3.10 grams acetanilide or 45.3% yield.

Ethyl acetate and aniline --220 degrees for 21 hours --173 grams acetanilide or 25.8% yield.

Phenyl acetate and aniline --220 degrees for 21 hours --3.21 grams acetanilide or 48.10% yield.

After knowing that the different esters and aniline would react it was planned to run a series of reactions at different temperatures and for different lengths of time. Two tables were to be filled out; one, the mixtures were to be heated in bomb tubes for twenty hours at different temperatures --100,150, 200 degrees centigrade. The second table consisted of heating the mixtures in bomb tubes at 200 degrees centigrade for different lengths of time --5, 10, 15 hours.

Methy Acetate and Aniline.

This reaction was first carried out 4.6 grams of methyl acetate and 4.7 grams of aniline were carefully weighed out and placed in a bomb tube. The mixture was calculated from the theoretical equation using one-sixteenth molar portion of methyl acetate and one-twentieth molar portion of aniline. No conceivable change could be detected when the two substances were mixed. Care had to be taken upon sealing the tube, as the work had to be done quickly or the tube would get hot enough to vaporize the methyl acetate and an explosion would result before the seal is completed. The tube was then carefully wrapped in paper and placed in the bomb furnace. The first run was for twenty hours at 100 degrees centigrade. After this time the furnace was allowed to cool and then the bomb removed. The mixture had turned dark and still liquid. The end of the tube was broken off and the mixture was washed out of the tube with alcohol into the "separating" apparatus. Then about twenty cc. of water was added and the acetanilide separated as before. The following different conditions were applied to the above mentioned mixture with the results as noted. Calculating from the amount

of aniline used in the reaction, theoretically 6.7 grams of acetanilide would be a 100% yield.

20 hours at 100 degrees centigrade yielded .60 grams or 8.9%.

20 hours at 150 degrees centigrade yielded .62 grams or 9.3%

5 hours at 200 degrees centigrade yielded 1.96 grams or 29.2%

10 hours at 200 degrees centigrade yielded 2.18 grams or 32.5%

15 hours at 200 degrees centigrade yielded 2.33 grams or 34.8

20 hours at 200 degrees centigrade yielded 2.89 grams or 43.1%

Ethyl Acetate and Aniline.

In this set of reactions 5.5 grams of ethyl acetate and 4.7 grams of aniline were used and placed in a bomb tube. There was only a slight darkening of the solution when the two substances were mixed. At the end of the run the solution was very dark and still liquid. The solution was washed into the "separating" apparatus with alcohol and steam distilled. Acetanilide began to separate out upon cooling to room temperature. The solution was concentrated, however, and cooled to the temperature of melting ice to be sure of complete crystallization.

The following different conditions were applied to this series of reactions with the results noted: (The percentage yield was computed on the basis of the quantity of aniline used.)

20 hours at 100 degrees centigrade yielded xxxx grams or xxxx %

20 hours at 150 degrees centigrade yielded .08 grams or 1.2 %

5 hours at 200 degrees centigrade yielded trace grams or trace %

10 hour at 200 degrees centigrade yielded 1.95 grams or 29.1%

15 hours at 200 degrees centigrade yielded 1.93 grams or 28.8%

20 hours at 200 degrees centigrade yielded 2.48 grams or 37.0%

Butyl Acetate and Aniline.

In this series of reaction 7.2 grams of butyl acetate and 4.7 grams were used in each bomb. No change was noted when the two substances were mixed. However at the end of the twenty hour run at 200 degrees centigrade and after cooling to room temperature, crystalls of acetanilide had formed in the mixture, which was then colored a dark brown. Calculations based on the amount of aniline used would give 6.7 grams of acetanilide for a 100% yield.

The following different conditions were applied to this series of reactions with the results noted:

20 hours at 100 degrees centigrade yielded trace

grams or trace %

20 hours at 150 degrees centigrade yielded .87 grams or 13.%

5 hours at 200 degrees centigrade yielded 1.50 grams or 22.4%

10 hours at 200 degrees centigrade yielded 2.39 grams or 35.7%

15 hours at 200 degrees centigrade yielded 2.82 grams or 42.1%

20 hours at 200 degrees centigrade yielded 3.27 grams or 48.8%

Phenyl Acetate and Aniline.

The quantities, 8.2 grams of phenyl acetate and 4.7 grams of aniline were used in this series of reactions. The mixture was placed in bomb tube, sealed and heated in the bomb furnace. The mixture turned dark immediately upon the addition of the ester to aniline. At the end of the time allowed for reaction the tubes were removed from the furnace and allowed to cool. The mixture crystallized and formed a black mass of crystals. The coloration being due to the formation of phenol during the reaction.

The top of the tube was broken off and the mixture washed out with alcohol into the "separating" apparatus until the distillate was clear. The residue in the flask was now emptied into a beaker and the phenol that stayed on the sides of the flask was washed into the beaker with alcohol. This mixture was boiled and some animal charcoal added with the boiling continued for about five minutes. After this time the solution was filtered while hot, concentrated and the acetanilide crystallized out at the temperature of melting ice. The product was very white and pure.

The following conditions were applied to this series of reactions with the results noted:

20 hours at 100 degrees centigrade yielded
5.72 grams or 85.3%

20 hours at 150 degrees centigrade yielded
5.80 grams or 86.6%

5 hours at 200 degrees centigrade yielded
5.70 grams or 85.0%

10 hours at 200 degrees centigrade yielded
5.95 grams or 88.17%

15 hours at 200 degrees centigrade yielded
6.00 grams or 89.6%

20 hours at 200 degrees centigrade yielded
6.18 grams or 92.1%

The Esters and Aniline with Catalysts.

Another series of reactions was planned with the use of a catalyist. Cuprous oxide was used in this case and added to the mixture of the ester and aniline in the bomb tube. Four bomb tubes were charged with their respective amounts of esters and aniline and two grams of the catalyst added to each tube. The tubes were then heated at 200 degrees centigrade in the bomb furnace for ten hours. After that time they were cooled and the mixture washed into the separating apparatus with alcohol preparatory to steam distillation. The catalyst was filtered from the residue in the distilling flask and concentrate. To that of phenal acetate some animal charcoal was first added and boiled for five minutes before filtering. After concentrating the acetanilide was crystallized from the mixture by cooling.

The following results were obtained:

Methyl acetate and aniline yielded 2.2 grams or 32.8%

Ethyl acetate and aniline yielded 1.93 grams or 28.8%

Butyl acetate and aniline yielded 2.44 grams or 36.1%

Phenyl acetate and aniline yielded 6.00 grams Or 89.6%

A catalyst did not appreciably influence

the reaction and further work on this series of reactions was discontinued.

Tabulated Results.

The following table gives the results of the work carried out for twenty hours at the temperature given. The results are in grams of acetanilide separated from the reacting mixture. Calculations based on the quantity of aniline used gives 6.7 grams of acetanilide as a 100% yiels.

20 hours.	Methyl	Ethyl acetate.	Butyl acetate	Phenyl A.
100 deg. A.	.60	none	trace	5.72
150 "	.62	.08	.87	5.80
200 "	2.89	2.48	3.27	6.18
200 degrees				
5 hours	1.96	trace	1.5	5.70
10 hours	2.18	1.95	2.39	5.95
15 hours	2.33	1.93	2.82	6.00

The following table gives the percentage reactions:

20 hours				
100 deg.	8.9	000	trace	85.3
150 deg.	9.3	1.2	3.0	86.6
200 deg.	43.1	37.0	48.8	92.1

5 hours	29.2	trace	22.4	85.0
10 hours	32.5	29.1	35.7	88.7
15 hours	34.8	28.8	42.1	89.6

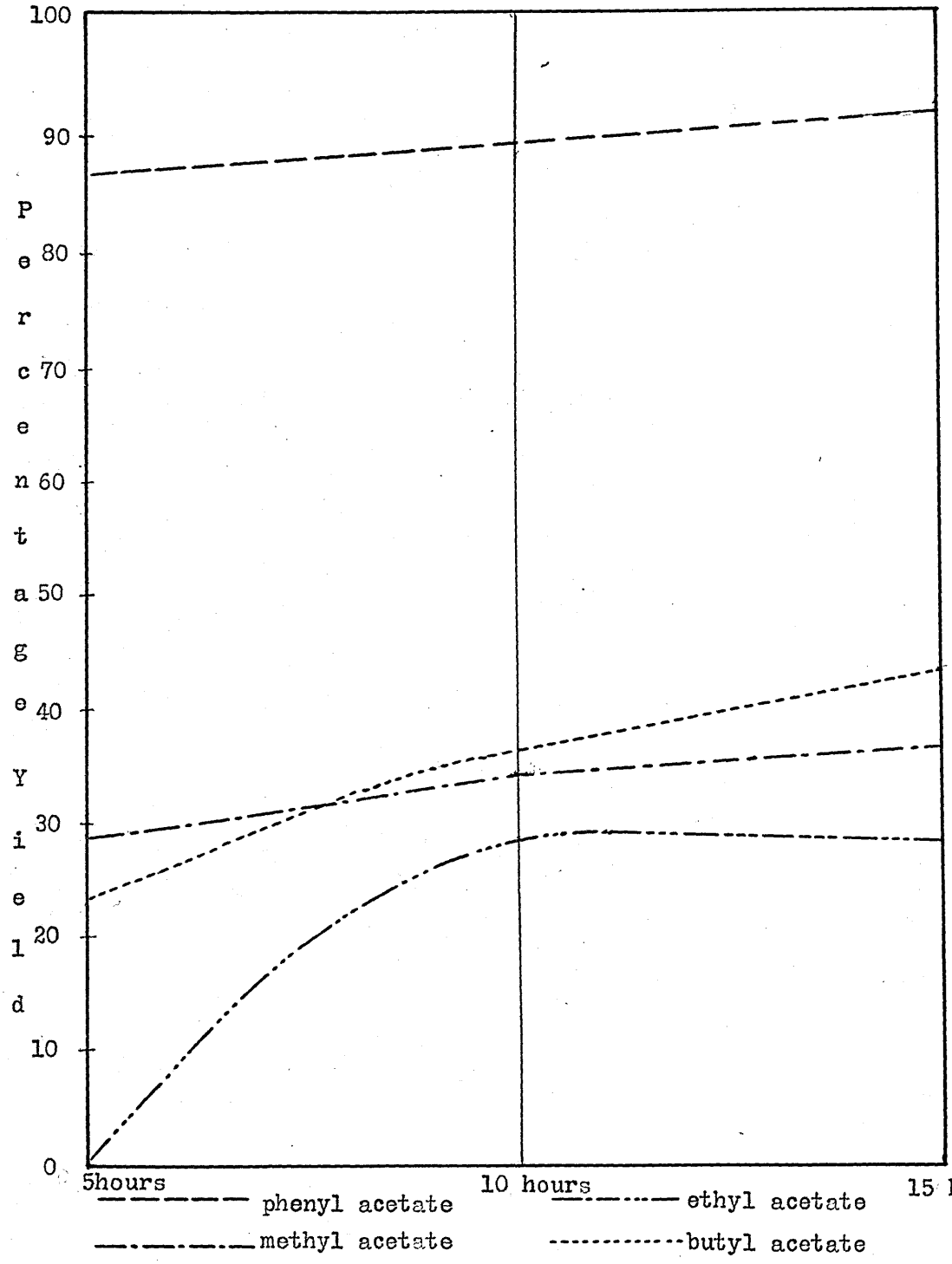
Summary.

The main object of this research was to ascertain the relative reactivity of the esters of acetic acid with aniline.

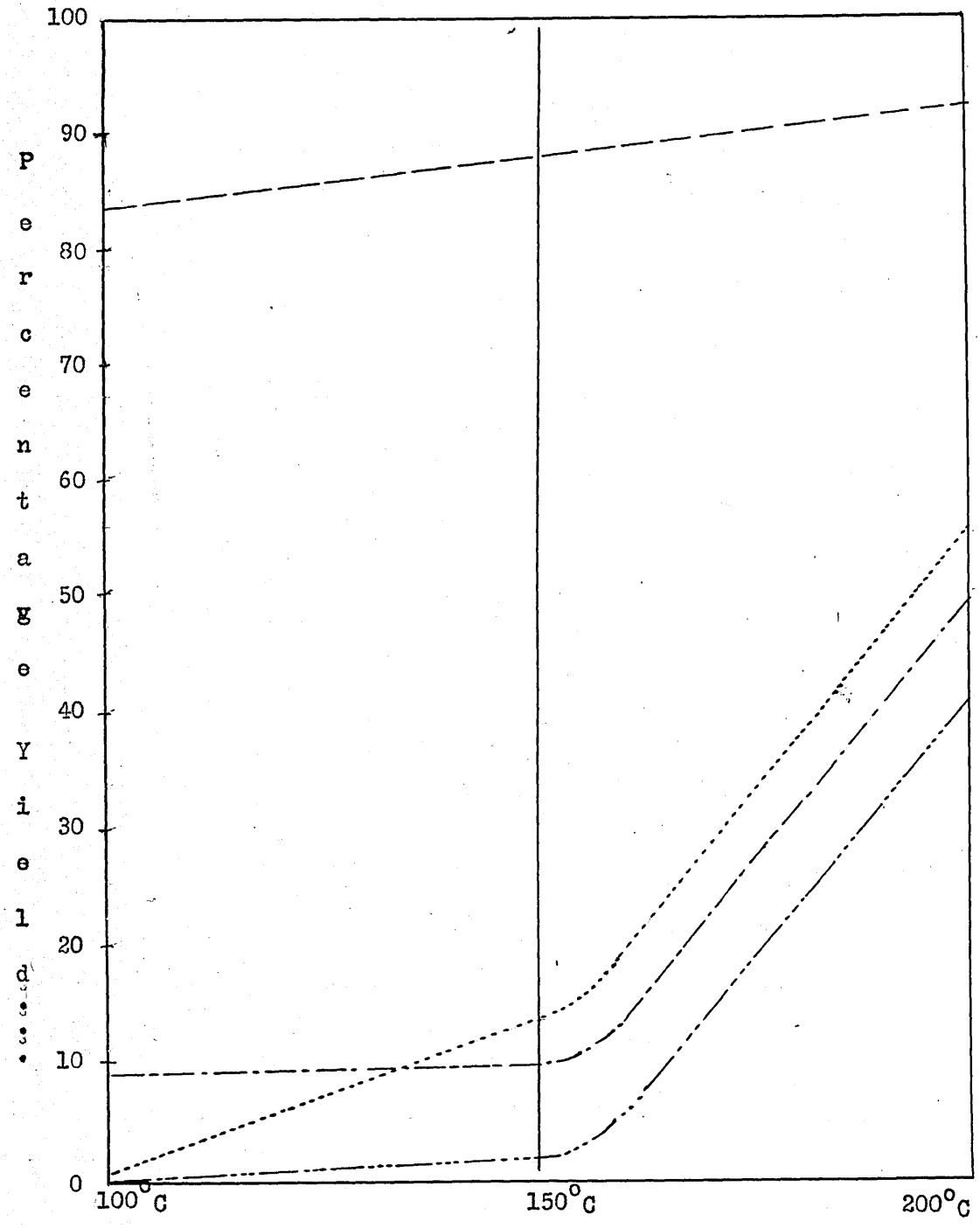
It was found that the esters would not interact with aniline at atmospheric temperature unless heated to at least 220 degrees centigrade for several days. The influence of pressure greatly increased the rate of reaction and care was taken to have the bomb tubes of the same diameter and same length.

The relative reactivity seems to follow directly with the molar weight of the ester, with the exception of the ethyl ester. Not enough research was done to trace the cause for such a deviation. However, it is possible that due to the greater power of ethyl acetate over that of butyl and phenyl acetate has caused a constraint on the system and lessened the rate of reaction. If true, this constraint was not relieved by the the addition of a catalyst-cuprous oxide. The relative great reactivity of phenyl acetate may be accounted for as due to the phenyl radical being negative and hydrolization is easily effected.

The phenyl ester shows an almost constant rate of reaction, while the methyl, ethyl, and butyl esters show a greater increase the higher the temperature and the longer the time of reaction; indicating that their extent of reactivity has not been reached.



Graph of the series of reactions at a constant temperature of 200 degrees centigrade.



Graph of the series of reactions carried out for a constant length of time. of 20 hours.