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A QUANTITATIVE STUDY OF THE ACTION OF MONOCHLORACETIC ACIDS UPON VARIOUS AMINES

A Thesis
by
Joseph Laurence Donnelly

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A Quantitative Study of the Action of Monochloracetic Acid Upon Various Amines.

I Introduction

The interaction of aniline and chloracetic acid, when heated together, is accompanied by the liberation of three gaseous products:- methyl chloride, carbon dioxide and hydrogen chloride. It is conceivable that the chloracetic acid may be the source of the carbon dioxide and methyl chloride according to the simple equation:

$$ClCH_2COOH \longrightarrow CH_3Cl + CO_2$$

The liberation of hydrogen chloride most likely accompanies the formation of phenyl glycine:

$$C_6H_5NH_2 + ClCH_2COOH \longrightarrow C_6H_5NHCH_2COOH + HCl.$$

This equation represents the common method of preparation of phenyl glycine.

No references were found in the literature relative to a quantitative study of the elimination of the three gases evolved in the interaction between chloracetic acid and aniline. Unfortunately the literature of organic chemistry too frequently fails to take into account the quantitative yields of the products of given reactions. The nature and, consequently, the description of any reaction is vitally deficient unless the investigation is <u>not only qualitative but also quantitative</u>.

Adopting this viewpoint, the present thesis is concerned

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with the study of the action of chloracetic acid upon aniline, methylaniline, dimethylaniline, ethylaniline and diethylaniline. In each of these reactions there is obtained carbon dioxide, hydrogen chloride and alkylchloride. It is, therefore, proposed, as the chief feature of this research, to devise methods for determining quantitatively the yields of each of these gaseous products in the several reactions.

In preliminary experiments it was found that a variation in the relative quantities of amine and acid gave varying yields of the gases mentioned. It was therefore determined, to study the action of chloracetic acid upon (1) aniline, (2) methylaniline, (3) monoethylaniline, (4) dimethylaniline, (5) diethylaniline; and with each of the five amines to study the reaction in four different molecular ratios of amine to acid, as follows: (A) two moles amine to one mole acid; (B) one mole amine to one mole acid; (C) one mole amine to two moles acid; (D) one mole amine to four moles acid.

II. Historical

There is nothing in the literature bearing upon any quantitative study of the gaseous products in the reaction between chloracetic acid and amines. The following reactions, which deal with the elimination of carbon dioxide during the decomposition of various substituted benzoic acids, have some bearing upon the present investigation. A brief review of those reactions is of interest.

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In 1892 Cazeneuve(2) announced that certain hydroxybenzoic acids are unstable, yielding carbon dioxide and phenol, when warmed with various amines. He found that on mixing gallic acid with about twice its weight of aniline, that the mixture suddenly solidified, and that this mass, when heated to 120°C, evolved carbon dioxide. At this temperature he was able to decompose all of the acid. Aniline pyrogallate separated on cooling.

Cazeneuve further found that liquid amines of the benzene series, notably o-toluidine, the xyledines and quinoline, behave in much the same way. Various phenolic acids have been found to eliminate carbon dioxide: protocatechuic acid decomposed at 180°, salicylic acid at 200°, while benzoic acid was unaffected. From this Cazeneuve drew the general conclusion that the stability of the carboxyl radical decreases as the number of phenolic hydroxyl radicals in the benzene nucleus increases.

On studying the decomposition of halogen substituted carboxylic acids, he found that dibromsalicylic acid decomposed at 180°, dichlorsalicylic acid at 200°, dibromgallic acid at 80° but that tribrombenzoic acid was unaffected. Also, methyldihydroxybenzoic acid lost CO at 110° while dibromsellenic acid did so only at 100°. Using as his criterion the temperature at which decomposition took place, he stated that the stability of acids was decreased through the substitution of halogen.

Hemmelmayr(3) extended this work and determined quantitatively the amount of carbon dioxide which a weighed amount of

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acid would yield when heated with either 50 cc of water or 50 cc of aniline for a definite period of time. He measured the stability of carboxyl groups in terms of the amounts of carbon dioxide evolved in given intervals of time. Various substituted benzoic acids were investigated. The four substituents which affected the stability of the carboxyl radical are arranged in the following descending order: OH, NO_2, Br, NH_2. Whenever ~~In each case in which~~ the carboxyl group was ortho or para to a hydroxyl group it yielded carbon dioxide, while, on the other hand, when carboxyl was meta to the hydroxyl it was stable. This held true with thirty-five out of thirty-nine hydroxybenzoic acids.

Still another example of this type of decomposition was reported in 1914 by Fry(4). He dissolved chlorcarbonicethylester in dry carbon tetrachloride and added pyridine. A white solid was immediately formed which soon decomposed into carbon dioxide and ethyl chloride. The extent of this decomposition:-

$$ClCOOC_2H_5 \xrightarrow{Pyridine} C_2H_5Cl + CO_2$$

was determined by absorbing the carbon dioxide in soda lime. Fry explained the liberation of carbon dioxide in terms of the polarity of the valences of the carbon in the carboxyl group, i.e., in terms of the electronic conception of valence.

These interesting researches of Cazeneuve, Hemmelmayr and Fry suggested the possibility of rendering the carboxyl of chloracetic acid unstable by heating with an amine.

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III. Method of Experiment.

A. The Reaction Mixture.

An accurately weighed quantity of chloracetic acid, approximately one tenth mole, was put into a 100 cc. long neck, round bottom flask and one fifth mole of aniline was added by means of a pipette. A white solid immediately formed and the reaction mixture became quite warm. The flask, connected to a spiral reflux condenser was immersed in a Wood's metal bath, in which a thermometer was suspended, and slowly heated. The solid The solid reaction mixture melted between 70° and 80°. At 150° an evolution of gas began which increased as the temperature was elevated. The temperature in this and in subsequent reactions was finally held at 250°. The gases, consisting chiefly of hydrogen chloride, carbon dioxide and methyl chloride, were found to contain traces of aniline and water vapor.

B. Purification of Gases Prior to Quantitative Absorption.

The first step in the quantitative estimation of these products of decomposition of chloracetic acid must be the elimination of aniline and water vapor, without concomitant loss of carbon dioxide, methyl chloride or hydrogen chloride. The first method which suggested itself was to pass the gases through concentrated sulphuric acid. While this proved satisfactory for the elimination of aniline and water, it held back appreciable amounts of methyl chloride through solution. The following experiment illustrated this point.

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To determine the extent of solubility of methyl chloride in sulphuric acid, methyl chloride was prepared by passing hydrogen chloride through boiling absolute alcohol and zinc chloride. The resulting gas was washed with water and then successively passed through soda lime, calcium chloride and sulphuric acid. When passed through 25.0 grams of concentrated sulphuric acid in a Liebig bulb, it was found that 0.4168 grams methyl chloride had been taken into solution. This experiment proves conclusively that sulphuric acid can not be employed to dry methyl chloride.

To test the suitability of calcium chloride as a drying agent methyl chloride was passed into a bulb containing 25 grams of dry, granular calcium chloride for fifteen mintues. The apparatus was first swept clear of any residual methyl chloride by a brisk stream of dry air, free from carbon dioxide, and then weighed. The bulb gained 0.0012 grams in weight, a negligable increase. Since it is well known that calcium chloride forms stable addition compounds with both water and amines, it satisfies all of the present requirements of a drying agent.

It then remained to devise a method for determination of carbon dioxide, hydrogen chloride and methyl chloride.

C. Simultaneous Absorption of Carbon Dioxide and Hydrogen Chloride.

A solution of potassium hydroxide was found to be impracticable for the absorption of carbon dioxide because it dissolved small amounts of methyl chloride. It was then decided to

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absorb the hydrogen chloride and the carbon dioxide simultaneously in soda lime. Fortunately, a Flemming bulb filled with soda lime was found to suffer no gain in weight when a brisk stream of methyl chloride was passed through it for fifteen minutes. Therefore, in the determinations which follow, the gain in weight of the soda lime bulb will represent the sum of the weights of the carbon dioxide and hydrogen chloride. But it is necessary to acertain these weights separately, i.e., devise means for determining the weight of hydrogen chloride absorbed. Knowing this, the weight of carbon dioxide absorbed may be found by difference. The description of the method of determining hydrogen chloride follows.

D. Determination of Hydrogen Chloride.

Although the determination of the quantity of the mixture of carbon dioxide and hydrogen chloride, as well as the quantity of methyl chloride, is accomplished from a given reaction mixture, it is necessary that hydrogen chloride be estimated from a separated execution of the experiment. Accordingly the mixture of chloracetic acid and amine was heated as before in a 100 cc. round bottom flask, connected with a spiral reflux condenser, but the evolved gases were passed directly into 50 cc. of a 30% solution of sodium hydroxide. Carbon dioxide, hydrogen chloride and some methyl chloride were absorbed in this operation. The caustic solution was diluted to 250 cc. and aliquot portions used for the determination of hydrogen chloride content.

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The dissolved methyl chloride was removed by warming the caustic solution in a beaker. This treatment effects practically no hydrolysis of methyl chloride, this being effected only under pressure. Carbon dioxide was easily eliminated on acidifying with nitric acid, and upon the addition of silver nitrate solution the hydrogen chloride was precipitated and weighed as silver chloride.

The various steps in the quantitative determination of carbon dioxide and hydrogen chloride may be summarized as follows. The evolved gas mixture containing traces of aniline and water vapor, carbon dioxide, hydrogen chloride and methyl chloride are passed through a spiral condenser and then into a U-tube containing granular calcium chloride. This absorbs the traces of aniline and water vapor but allows the other gases to pass on without alteration in quantity. They next pass into a weighed Fleming bulb containing small grained soda lime which effects the simultaneous absorption of carbon dioxide and hydrogen chloride, without loss of methyl chloride. Hydrogen chloride is determined by passing the gases, evolved from a separate reaction mixture of the same relative molecular quantities of amine and acid, through a solution of socium hydroxide and weighing hydrogen chloride as silver chloride.

E. <u>Determination of Methyl Chloride</u>.

Since the interior volume of the entire apparatus in these experiments is approximately 200 cc., it is evident that there will be quite an error unless precautions are taken to

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sweep out any gases, which would otherwise remain in the system. To this end, at the close of each determination, air was passed through the entire apparatus until the last traces of the gases had been swept out. Hence, the absorbents chosen for the various gases must be of such a nature that they are uneffected by the presence of fairly large volumes of dry air, free from carbon dioxide. Moreover, the absorbent for methyl chloride must not lose same when air is passed through it. The methods already chosen for the absorption of carbon dioxide and hydrogen chloride conform to these requirements, since their retention is through chemical interaction with their absorbing medium. The problem next to be encountered was the quantitative determination of methyl chloride through complete absorption in a medium which fulfils the requirments noted above.

1. Methods Already Proposed in the Literature for the Absorption of Methyl Chloride.

Allison and Meighan(5) mention three methods of determining methyl chloride in various gas mixtures. First, they suggest condensation and fractional distillation of the gas at low temperatures. This would evidently be a slow and difficult method, the accuracy of which would be greatly lessened by the presence of much air. Therefore, it was not feasible in the present research. Secondly, they suggest combustion of methyl chloride in the presence of a platinum spiral, and absorption of the resultant gases by caustic. It was assumed that the methyl

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chloride would burn according to the following equation:

$$2CH_3Cl + 3O_2 \longrightarrow 2CO_2 + 2HCl + 2H_2O$$

They claim that the temperature needed for the combustion is so high that the platinum spiral lasts only a short time. It is evident that this method is impractical in the present investigation.

Finally, they suggest the absorption of methyl chloride in glacial acetic acid. They measured an air mixture of methyl chloride in a gas burette and then passed it six times back and forth through a Hemple pipette containing glacial acetic acid. It was then returned to the burette and from the contraction in volume the percentage of methyl chloride was calculated. The large volume of air, needed in the present determination to sweep out the apparatus, renders this method impracticable.

A brief account of attempts to effect absorption of methyl chloride in various substances follows.

2. <u>Glacial Acetic Acid</u>.

The solubility of methyl chloride in glacial acetic acid suggested the possibility of absorbing it directly in a weighed Liebig potash bulb. A Liebig bulb was filled with glacial acetic acid, 23.71 grams, and the outlet fitted with a tube containing soda lime and calcium chloride. The acid was found to absorb 2.5410 grams of methyl chloride at room temperature. But to fill the present requirements the gas so held in solution must not be removed on passage of air through the system. To test this requirement dry carbon

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dioxide free air, at the rate of 100 cc. per minute, was passed through the weighed Leibig bulb containing the glacial acetic acid previously saturated with methyl chloride. The loss of weight which represents the weight of methyl chloride removed by the air, is shown in the following table.

Time (Minutes)	Volume of air (cc.)	CH_3Cl removed. (gm.)
1	100	0.3400
3	300	0.8104
5	500	1.1011

From these figures it is apparent that the loss of methyl chloride from glacial acetic acid, on passage of air through it, is too great to warrant its use as an absorbent. It may be seen that the successive loss of methyl chloride per minute decreases. That is, as the concentration of the solution of methyl chloride in acetic acid decreases, the loss through removal by air also decreases. The loss from a dilute solution should be quite small.

The possibility of reabsorbing the removed methyl chloride by passing it through a second Liebig bulb of acetic acid was investigated as follows. A second bulb, containing glacial acetic acid, carefully weighed, was attached to the outlet tube of a bulb filled with glacial acetic acid previously saturated with methyl chloride. Air at the rate of 100 cc. per minute was then forced through both bulbs, so that any methyl chloride removed from the first bulb might be reabsorbed in the second. The tabulated results follow.

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Time (Min.)	Vol. air.	Wt. CH_3Cl excluded from bulb I. (gm.)	Wt. CH_3Cl reabsorbed in bulb II (gm.)
1	100	0.4323	0.4160
3	300	0.9013	0.8025
6	600	1.5200	1.1172

There was a total loss of 0.4028 grams in six minutes. Therefore, this plan had to be abandoned.

The results obtained with other absorbents should be noted.

3. Acetic Ethyl Ester.

15 grams of acetic ethyl ester were found to gain 1.9483 grams in weight when methyl chloride was passed through it to the saturation point. But the absorbent itself was found to be too volatile to serve the purpose.

4. Glycerine.

On the other hand, non-volatile glycerine absorbed only 1.3% of its own weight of methyl chloride at room temperature. This would necessitate the use of too large a volume of absorbent. It also was discarded.

5. Petroleum Oil.

The absorbing qualities of light petroleum oil was next investigated. 10.8755 grams of this oil were placed in a Liebig bulb and methyl chloride passed through it. At the end of fifteen minutes there was only 0.2601 grams gain in weight. Petroleum oil is therefore useless.

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6. Alcohol.

Ethyl alcohol absorbed four times its own volume of the gas, but like acetic ethyl ester was too volatile for use.

7. Lloyd's Reagent.

Lloyd's Reagent, an aluminium silicate, was suspended in a Fleming bulb with plugs of loose cotton. After passage of a brisk stream of methyl chloride through this for an hour, it was found to suffer no gain in weight.

8. Cocoanut Charcoal.

Finally a thorough investigation of the absorption of methyl chloride by a specially prepared cocoanut charcoal was undertaken. The charcoal (40 minute chlorpicrin activity) was first ignited in a covered iron crucible and then allowed to cool for several hours in a dessicator over calcium chloride, at atmospheric pressure. After this treatment it was found that it did not gain in weight when dry carbon dioxide free air was passed through it. It is the object of the following experiments to ascertain (1) the extent of the absorption of methyl chloride by charcoal, and (2) the effect of the passage of air through charcoal saturated with methyl chloride.

41.50 grams of cocoanut charcoal in a Fleming bulb with methyl chloride gained 9.743 grams in weight when completely saturated at room temperature and pressure. When, however, air was passed through the bulb at the rate of 100 cc. per minute, the loss in weight which the charcoal suffered

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through removal of methyl chloride, was as follows:

Time (Min.)	Vol. air. (cc.)	CH_3Cl removed (gm.)	Percent loss
1	100	0.0716	0.73
2	200	0.1542	1.58
5	500	0.3680	3.77
10	1000	0.6743	6.92

From the foregoing table it is evident that one liter of dry, carbon dioxide free air, passed through 41.50 gm. charcoal, saturated with 9.743 grams of methyl chloride, effects a loss of 0.6743 grams of methyl chloride or 6.92% of the absorbed gas.

Since it is necessary to sweep through the apparatus and to retain through absorption all of the methyl chloride which has been formed, the object of the following experiment is to determine how much of the methyl chloride so removed, can be recovered when it is subsequently passed through a second mass of fresh charcoal.

To a bulb of charcoal, saturated with methyl chloride, a second bulb of fresh charcoal was connected. When air was then passed through the system any methyl chloride removed from the first bulb would be reabsorbed in the less saturated charcoal of the second bulb. 600 cc. of air were passed through the system in six minutes. The data follows.

Time (Min.)	Vol. air cc.	Loss CH_3Cl Bulb I (gm.)	Gain CH_3Cl Bulb II (gm.)
6	600	0.4401	0.4335

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There was a total loss of only 0.0066 gm. methyl chloride or approximately 0.06% of the total amount of gas absorbed.

Evidently, methyl chloride is easily removed from charcoal by air, when the charcoal is very highly saturated. When, however, another mass of fresh charcoal is connected to the system, the excluded methyl chloride comes in contact with the fresh absorbent, is reabsorbed, and perhaps held more firmly because of the low concentration of the gas in the charcoal in the second bulb. If it is again removed by the air, it immediately comes in touch with unsaturated absorbent further on in the bulb, and is retained.

The foregoing result suggested the study of the effect of the passage of air through large U-tubes of charcoal approximately one half saturated with methyl chloride. A large U-tube was filled with 40.00 grams of charcoal. Methyl chloride was passed through this until there was a gain in weight of 3.8215 grams. It was then less than half saturated. It was naturally assumed that the inlet region of the tube was saturated with methyl chloride while the sections of the charcoal further removed were practically free from it. This would mean that approximately 15. cm. length of the U-tube held methyl chloride and that this was followed by about 30 cm. length of charcoal for the reabsorption of any gas which would be carried out of the saturated area. Air was passed through the U-tube at the rate of 100 cc. per minute. Any loss of methyl chloride would be equal to the loss in weight of the tube. This

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was determined by weighing at different intervals. The data is as follows:

Trial I

40.00 gm. charcoal containing 3.8215 gm. CH_3Cl.

Time (Min.	Vol. air. (cc.)	Loss weight. (gm. CH_3Cl.)
1	100	0.0008
2	200	0.0013
3	300	0.0021
6	600	0.0052

Trial II

40.00 gm. charcoal containing 4.6286 gm. CH_3Cl.

Time (Min.)	Vol. air. (cc.)	Loss weight. (gm. CH_3Cl.)
1	100	0.0024
2	200	.0056
3	300	.0075
4	600	.0136

This represents a total loss of 0.13% in the first trial and 0.29% loss in the second. This proves that this method is feasible. It was then decided to use charcoal contained in large U-tubes as the absorbent for methyl chloride, and to always so choose the amount of charcoal, that if the chloracetic acid would give 100% decomposition, it would only be half saturated with the methyl chloride evolved.

The following diagram represents the apparatus used in the experiments which follow.

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F. Manipulation.

The reaction mixture of amine and acid was placed in a 100 cc. round bottom, long neck flask A (see figure), fitted with a two hole cork and spiral reflux condenser B. The second hole of the cork was fitted with a glass tube C drawn to a fine bore, extending into the rounded portion of the flask. The outer end of this tube was closed with a piece of rubber tubing and a screw clamp D. The reflux condenser was connected with a U-tube E which is partly filled with calcium chloride and loosely plugged with cotton. The outlet from this drying tube was connected with a Fleming bulb, the absorbing section F of which was filled with small grained soda lime, the drying section G, with calcium chloride. This in turn was connected with a large U-tube H filled with charcoal and protected by a small portion of calcium chloride at the outlet.

The reaction mixture in the flask, submerged in the Wood's metal bath I, was slowly heated for a space of thirty minutes until a temperature of 250°C was obtained. It was then held at 250°C for two hours. At the end of this time the flask was allowed to cool, and for six minutes dry carbon dioxide free air was forced through the capillary tube C, which extended into the flask. The air was measured by means of a flowmeter and sent through the apparatus at the rate of 100 cc. per minute. This insured the absorption of all gases which otherwise would not have come in contact with the absorbing materials.

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The gain in weight of the Fleming bulb represents the sum of the weights of carbon dioxide and hydrogen chloride. The weight of methyl chloride evolved, is represented by the gain in weight of the charcoal tube H.

In determining the hydrogen chloride, the tube from the condenser was directly connected with two gas washing bottles equipped with special bubbling attachments, each bottle containing 50.0 cc. of 30% sodium hydroxide solution. Another reaction mixture of amine and acid was heated for two hours at a temperature of 250°C as previously described. The apparatus was swept out with air at the rate of 100 cc. per minute to insure the passage of all of the hydrogen chloride through the sodium hydroxide. The contents of the bottles were diluted to 250 cc. and aliquot portions analyzed for hydrogen chloride content as follows.

The caustic solution was heated to insure removal of any methyl chloride and the carbonates were decomposed by addition of dilute nitric acid. Finally the hydrogen chloride was precipitated and weighed as silver chloride.

Calculations.

The amount of carbon dioxide may be calculated by difference, thus:

Ascertain the combined weight of carbon dioxide and hydrogen chloride simultaneously evolved from a reaction mixture containing a given molar ratio of chloracetic acid and amine.

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Subtract from this the amount of hydrogen chloride determined from a second reaction mixture containing the same ratio of amine and acid.

The percentages of carbon dioxide and methyl chloride evolved from each reaction mixture investigated, were calculated by referring the actual yields of these substances to the amounts which would have been liberated had the chloracetic acid been fully decomposed according to the equation:

$$ClCH_2O_2H \longrightarrow CH_3Cl + CO_2 .$$

On the other hand, the percentage of hydrogen chloride was calculated on the basis of the following equation:

$$RNH_2 + ClCH_2CO_2H \longrightarrow RNHCH_2CO_2H + HCl .$$

The weight of hydrogen chloride actually obtained was compared with the weight which would have been evolved had all of the chloracetic acid reacted according to the above equation which will frequently be referred to as the glycine reaction.

Due to the difficulty in handling the very hygroscopic chloracetic acid, it was impossible to weigh exactly the same amount of acid in the determination of the hydrogen chloride alone as in that of the combined hydrogen chloride and carbon dioxide mixture. Hence, to render comparable the respective yields of hydrogen chloride and carbon dioxide it was necessary to calculate the amount of hydrogen chloride which the chloracetic acid would have yielded in the combined carbon dioxide hydrogen chloride determination.

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The following data will illustrate the method of calculation. 10.00 grams chloracetic acid, when heated with aniline in the ratio of two moles of aniline to one mole of chloracetic acid gave 0.6668 grams total of carbon dioxide and hydrogen chloride. The charcoal tube increased 0.0579 grams in weight which represents the weight of methyl chloride evolved.

10.78 grams of chloracetic acid yielded 0.0014 grams of hydrogen chloride when heated with aniline in the same molar ratio. By calculation from the proportion 10.78:10.00 =.0014:x, it is found that 10.00 grams of chloracetic acid would yield (x) or 0.0013 grams of hydrogen chloride. Subtracting this weight of hydrogen chloride (0.0013), from the total weight of hydrogen chloride and carbon dioxide evolved from 10.00 grams of chloracetic acid (0.6668), gives the actual weight of carbon dioxide evolved, namely 0.6655 grams.

The theoretical percentage of Carbon dioxide, methyl chloride and hydrogen chloride as calculated from the ratios $ClCH_2CO_2H:CO_2$, $ClCH_2CO_2H: CH_3Cl$, and $ClCH_2CO_2H:HCl$, are respectively 14.20% CO_2, 1.00% CH_3Cl and 0.03% HCl.

IV. Specific Reactions Investigated and Data.

It has been observed that a variation in the relative quantities of a given amine and chloracetic acid gave varying yields of the gases in question. In this section the characteristic behavior of each of the amines is briefly described and all of the quantitative data is tabulated.

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Reaction I. Chloracetic Acid and Aniline.

The addition of aniline to chloracetic acid, in each of the four reaction mixtures, was characterized by the formation of a white compound. The reaction was exothermal. The reaction mixture was found to melt at temperatures which varied with the relative amount of amine and acid brought together. When the temperature was raised above the melting point, an evolution of the gases began, the rate of which increased as the ratio of amine to acid diminished. The reaction mixture at the end of the experiment was an amber colored, rubber like mass, except in the case when the ratio was of four moles of acid to one mole of amine. In this instance it was black.

The following data (Table I), presents the quantities of carbon dioxide, methyl chloride and hydrogen chloride evolved by a given amount of chloracetic acid when heated with aniline in the several ratios:(A) two moles aniline to one mole chloracetic acid, (B) one mole aniline to one mole chloracetic acid, (C) one mole aniline to two moles chloracetic acid, (D) one mole aniline to four moles chloracetic acid. It should be noted under each of the several reaction ratios (A,B,C,D) that four experimental determinations (a',b',a",b") were made. The quantitative determinations a' and a" are duplicate checks in which the carbon dioxide and hydrogen chloride were simultaneously absorbed and subsequently weighed in the Fleming bulb, while the alkyl halide was absorbed and likewise subsequently weighed in the U-tube containing the cocoanut charcoal. Determinations b' and b" are duplicate check experiments in which the

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the quantity of hydrogen chloride evolved was separately determined by absorption in sodium hydroxide solution as previously described.

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Table I. Aniline and Chloracetic Acid.

	Amine (gm.)	Chlor acetic acid (gm.)	HCl+CO$_2$ (gm.)	HCl (gm.)	CO$_2$ (gm.)	CH$_3$Cl (gm.)	Percent Theory HCl.	Percent Theory CO$_2$.	Percent Theory CH$_3$Cl.
A	2	1							
'	19.70	10.00	0.6668	0.0013	0.6655	0.0579	0.03	14.2	1.0
'	21.20	10.78		0.0014					
"	18.72	9.50	0.5359	0.0022	0.5337	0.0424	0.06	12.2	0.83
B	1	1							
'	10.59	10.75	2.2605	1.2628	0.9977	0.2009	30.6	19.9	3.5
'	11.19	11.25		1.3207					
"	10.46	10.62	2.1530	1.2247	0.9283	0.1892	29.8	18.7	3.3
"	10.70	10.95		1.2628					
C	1	2							
'	4.92	10.00	4.3042	2.1245	1.8605	0.4488	54.9	39.9	8.4
'	5.72	11.63		2.4707					
"	5.40	11.63	4.6024	2.3802	2.3802	2.2222	53.0	41.0	9.0
"	6.02	12.23		2.5030					
D	1	4							
'	2.60	10.72	4.9145	2.5251	2.3894	1.1465	61.1	47.9	20.0
'	2.60	10.72		2.5251					
"	2.40	8.68	4.0150	2.0311	1.9839	1.0200	60.2	49.1	21.9
"	2.23	9.10		2.1365					

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Reaction II. Methyl Aniline and Chloracetic Acid.

The addition of methyl aniline to chloracetic acid was not accompanied either by formation of a solid addition compound or noticeable change in termperature. The amine dissolved a part of the acid in the cold: the remainder went into solution on application of heat. The initial evolution of hydrogen chloride, carbon dioxide and methyl chloride was so vigorous that the heating had to be done with caution. The reaction mixture, at first a yellow liquid, finally had the appearance of a red viscous oil.

The data which follows (Table II), presents the amounts of hydrogen chloride, carbon dioxide and methyl chloride yielded by chloracetic acid when heated with methyl aniline in the four different reaction ratios,(A,B,C, and D) and pairs of duplicate checks a',b',and a",b", described in preceding Reaction I.

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Table II. Methyl Aniline and Chloracetic Acid.

Amine (gm.)	Chlor acetic acid.	$HCl+CO_2$ (gm.)	HCl (gm.)	CO_2 (gm.)	CH_3Cl (gm.)	Percent Theory HCl.	Percent Theory CO_2.	Percent Theory CH_3Cl.
2	1							
23.20	10.71	2.2540	0.0115	2.2425	1.1445	0.27	44.9	20.0
23.20	10.71		0.0115					
35.36	15.65	3.3826	0.0335	3.3491	1.7435	00.55	45.9	20.9
22.23	9.84		0.0211					
1	1							
13.60	11.98	3.2387	0.2642	2.9745	4.0210	5.7	53.2	62.8
12.53	11.06		0.2440					
12.53	11.06	2.9081	0.2440	2.6641	3.7233	5.7	51.7	63.0
12.47	11.00		0.2427					
1	2							
9.29	16.46	6.1015	1.5692	4.5323	5.5530	24.7	59.3	63.1
5.95	10.51		1.0023					
9.54	16.84	6.1855	1.5603	4.6252	5.6420	24.1	58.9	62.7
6.12	10.85		1.0053					
1	4							
3.06	10.84	4.6043	1.3911	3.2132	3.2975	33.2	63.6	56.9
2.68	9.53		1.2230					
2.80	10.00	4.2856	1.2004	3.0852	3.0992	31.1	66.2	58.0
2.68	9.53		1.440					

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Reaction III. Monoethyl Aniline and Chloracetic Acid.

When ethyl aniline was mixed with chloracetic acid, a part of the acid went into solution but no solid addition compound was formed. On heating, the complete solution of the acid in the amine was followed by a brisk evolution of the three gases. The initial heating in this instance also had to be done with caution.

The percentage of hydrogen chloride, carbon dioxide and alkyl chloride evolved from the four ratios of ethyl aniline and chloracetic acid are embodied in the following Table III.

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Table III. Mono Ethyl Aniline and Chloracetic Acid.

	Amine (gm.)	Acid (gm.)	CO_2+HCl (gm.)	HCl (gm.)	CO_2 (gm.)	Alkyl Chloride (gm.)	Percent Theory HCl.	Percent Theory CO_2.	Percent Theory Alkyl Chloride.
A	2	1							
"	25.60	9.83	1.8570	0.0252	1.8292	3.8950	0.66	40.0	74.1
"	27.20	10.60		0.0272					
"	20.82	8.12	1.5900	0.0157	1.5743	3.2975	0.50	41.6	76.0
"	26.4	10.29		0.0200					
B	1	1							
"	15.37	10.93	2.6570	0.1169	2.5401	4.8795	2.7	49.9	83.5
"	12.74	9.91		0.1060					
"	14.49	11.36	2.7135	0.1296	2.5839	5.0335	2.9	48.8	32.9
"	13.80	10.07		0.1149					
C	1	2							
"	7.31	11.43	4.0265	0.9678	3.0587	4.8375	21.9	57.4	79.2
"	6.40	10.06		0.8511					
"	6.80	10.67	3.8425	0.8989	2.9436	4.6505	21.8	59.2	81.0
"	7.05	11.00		0.9361					
D	1	4							
"	3.63	11.29	4.9785	1.8023	3.1762	3.2282	41.3	60.3	53.5
"	2.95	9.20		1.4687					
"	3.37	10.50	4.7425	1.6918	3.0507	3.1289	41.7	62.5	55.6
"	3.29	10.27		1.6548					

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Reaction IV. Dimethyl Aniline and Chloracetic Acid.

The mixing of chloracetic acid and dimethyl aniline was not characterized by any visable chemical change. A small part of the acid dissolved in the amine but no solid addition compound was formed. On application of heat the chloracetic acid completely dissolved forming a yellow liquid. Further elevation of temperature caused the solution to pass through an interesting series of color changes: from yellow to green, from green to purple, and finally to red. At the end of the experiment the reaction mixture was a red viscous oil.

The following Table IV presents the amounts of the various gases produced in each of the four different molar ratios of acid to amine.

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Table IV. Dimethyl Aniline and Chloracetic Acid.

mine. gm.)	Acid. (gm.)	HCl+CO$_2$ (gm.)	HCl (gm.)	CO$_2$ (gm.)	CH$_3$Cl (gm.)	Percent Theory. HCl.	Percent Theory CO$_2$	Percent Theory CH$_3$Cl
2	1							
.34	9.48	1.0645	0.0148	1.0497	4.8060	0.39	22.8	90.9
.62	9.89		0.0155					
.55	9.80	0.9989	0.0154	0.9835	4.8757	0.04	21.5	93.1
.20	10.50		0.0165					
1	1							
.48	11.23	1.9676	0.0242	1.9434	5.6952	0.5	37.1	94.6
.06	10.15		0.0219					
.88	10.81	1.8610	0.0231	1.8369	5.4470	1.58	36.5	94.3
.25	10.24		0.0219					
1	2							
.03	10.92	2.7505	0.1021	2.6484	5.3395	2.4	52.8	91.5
.6	10.23		0.0957					
.97	12.34	3.0280	0.1154	2.9126	6.2261	2.40	50.7	94.4
.6	10.23		0.0957					
1	4							
.16	9.80	3.6385	0.8979	2.7406	3.7250	23.7	60.1	71.1
.09	9.65		0.8842					
.30	10.32	3.8464	0.9007	2.9457	4.1491	22.5	61.2	71.0
.20	10.00		0.8726					

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Reaction V. Diethyl Aniline and Chloracetic Acid.

The mixing of chloracetic acid and diethyl aniline gave no visible evidence of chemical reaction. When, however, the mixture was heated, it became red in color and alkyl chloride, hydrogen chloride and carbon dioxide were evolved.

The amounts of these gases obtained in the various reaction mixtures are embodide in Table V.

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Table V. Diethyl Aniline and Chloracetic Acid.

Amine (gm.)	Acid (gm.)	CO_2 +HCl (gm.)	HCl (gm.)	CO_2 (gm.)	Alkyl Chloride (gm.)	Percent Theory.	Percent Theory.	Percent Alkyl Chloride Theory.
2	1							
16.39	5.19	0.3110	0.0026	0.3084	3.2948	0.1	12.7	118.8
32.40	10.46		0.0053					
32.94	10.81	0.5200	0.0052	0.5148	6.7485	0.12	10.2	116.8
32.67	10.63		0.0051					
1	1							
15.50	9.82	1.1045	0.0028	1.1017	6.1851	0.07	24.0	117.8
15.63	9.90		0.0028					
16.50	10.45	1.1563	0.0026	1.1537	6.5041	0.06	23.7	116.4
15.70	9.92		0.0025					
1	2							
10.98	13.91	2.7110	0.5234	2.1876	7.8425	9.7	33.7	104.1
7.82	9.95		0.3774					
9.47	12.01	2.3704	0.4498	1.9206	6.7906	9.7	34.3	105.8
10.25	13.00		0.4869					
D 1	4							
3.19	08.16	3.0081	0.8388	2.1693	2.9173	26.6	57.0	66.9
3.95	10.00		1.0283					
5.29	13.40	4.8919	1.3798	3.5131	4.8025	26.7	56.3	67.0
3.96	10.01		1.0315					

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The table which follows summarizes the contents of the preceeding tables I - V, and presents the average yield of the two determinations for each of the reaction ratios: (A) two moles amine to one of chloracetic acid; (B) one mole amine to one of acid; (C) one mole amine to two of acid; (D) one mole amine to four of chloracetic acid.

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I. Ratio Aniline Amine to Acid		%CO	%CH Cl	%HCl
A	2:1	13.2	.90	.04
B	1:1	19.2	3.40	30.2
C	1:2	40.4	8.70	53.9
D	1:4	48.5	20.90	60.6
II Ratio Methyl Aniline Amine to Acid				
A	2:1	45.4	20.4	.41
B	1:1	52.4	62.9	5.7
C	1:2	59.1	62.9	24.4
D	1:4	64.9	57.4	32.1
III Mono Ethyl Aniline Alkylchloride				
A	2:1	40.8	75.0	.58
B	1:1	49.3	83.2	2.8
C	1:2	58.4	80.1	21.8
D	1:4	61.4	54.5	41.5
IV Ratio Dimethyl Aniline Amine to Acid				
A	2:1	22.1	92.0	.4
B	1:1	36.8	94.4	.5
C	1:2	51.7	92.9	2.4
D	1:4	60.8	71.0	23.1
V Di Ethyl Aniline Alkylchloride				
A	2:1	11.4	117.8	.1
B	1:1	23.8	117.1	.06
C	1:2	32.0	104.9	9.7
D	1:4	56.6	66.8	26.6

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General Summary of Data.

A general survey of this data shows that in each of the five reactions studied, the amounts of carbon dioxide and hydrogen chloride evolved increases as the ratio of amine to acid decreases. The yields of alkyl chloride do not follow this regularly except in Reaction I, i.e., aniline and chloracetic acid, in which there is a steady increase in the amount of methyl chloride as the ratio of amine to acid decreases. In Reactions II, III and IV (monomethyl aniline, monoethyl aniline and dimethyl aniline) the quantity of alkyl chloride increases through the ratios A and B (ratios 2 amine : 1 acid, and 1 amine : 1 acid). But in ratios C and D, (ratios 1 amine : 2 acid, and 1 amine : 4 acid) the yields of alkyl chloride decrease. In reaction V, alkyl chloride decreases through the four ratios A,B,C and D.*

The problem now presented is to explain not only the evolution of these gases, hydrogen chloride, alkyl chloride and carbon dioxide, but their varying yields in the four reaction mixtures.

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* It is apparently anomalous that the percentage yields of alkyl chloride in ratios A,B,C and D are greater than 100 %. This anomaly will be explained later.

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In the following discussion, a number will be assigned to each equation for every possible reaction which may be assumed to have taken place. The number of the given equation (or reaction) will be convenient for reference throughout the proposed interpretations.

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V. Interpretation of Data.

Reaction I. Aniline and Chloracetic Acid.

Before proceeding to a more specific discussion of the data obtained in the performance of the reaction between aniline and mono-chloracetic acid, the equations representing all of the possible reactions which might effect the elimination of carbon dioxide, methyl chloride and hydrogen chloride will be considered.

1. $CH_2ClO_2H \longrightarrow CH_3Cl + CO_2$
2. $C_6H_5NH_2 + CH\ ClCO\ H \longrightarrow C_6H_5NHCH_2CO_2H + HCl$
3. $C_6H_5CHCH_2CO_2H + CH\ ClCO\ H \longrightarrow C_6H_5N(CH_2CO_2H)_2 + HCl$
4. $C_6H_5NHCH_2CO_2H \longrightarrow C_6H_5NHCH_3 + CO_2$
5. $C_6H_5N(CH_2CO_2H)_2 \longrightarrow C_6H_5N(CH_3)_2 + 2CO_2$
6. $C_6H_5NHCH_3 + CH_2ClCO_2H \longrightarrow C_6H_5NCH_3CH_2CO_2H + HCl$
7. $C_6H_5NCH_3CH_2CO_2H \longrightarrow C_6H_5N(CH_3)_2 + CO_2$
8. $C_6H_5NH_2 + CH_3Cl \longrightarrow C_6H_5NCH_3H + HCl$
9. $C_6H_5NHCH_3 + CH_3Cl \longrightarrow C_6H_5N(CH_3)_2 + HCl$
10. $C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_2 . HCl$
11. $C_6H_5NHCH_3 + HCl \longrightarrow C_6H_5NHCH_3 . HCl$
12. $C_6H_5N(CH_3)_2 + HCl \longrightarrow C_6H_5N(CH_3)_2 . HCl$

Equations 1 to 7 represent all of the possible reactions which may produce any of the three gases. Equations 8 to 9 involve a possible consumption of methyl chloride, but the hydrogen chloride so produced may be held back as the hydrochloride of the amine. Equations

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10,11 and 12 represent retention of hydrogen chloride through the formation of amine salts. These last three reactions would only be expected in the presence of an excess of amine.

Specific assumptions and conclusions will be made from the point of view of the foregoing twelve reactions in conjunction with the quantitative data in Table I.

<u>Ratio A.</u> <u>Reaction I.</u>

Carbon dioxide is the only volatile product eliminated in appreciable quantity, 13.3 %. Methyl chloride and hydrogen chloride are produced in quantities of less than one percent. If the source of carbon dioxide is through the catalytic reaction (1), then the methyl chloride must have been appropriated according to reaction 8. It is, however, more likely that the glycine reaction, (2), predominated and that 13.2 % carbon dioxide is to be attributed to a decomposition of glycine according to reaction 4. Absence of hydrogen chloride is readily explained by the reaction numbered 10, indicating the formation of aniline hydrochloride, since there is an excess of aniline present in this reaction mixture.

If, in reaction-mixture A, reactions numbered 2, 4 and 10 proceed simultaneously and independently, the following equation is derivable.

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$2C_6H_5NH_2 + ClCH_2CO_2H \longrightarrow C_6H_5NH_2 \cdot HCl + C_6H_5NHCH_3 + CO_2$

This equation accounts very well for the elimination of carbon dioxide, and the absence of free hydrogen chloride in this experiment.

Ratio B. Reaction I.

In this ratio of one mole chloracetic acid to one mole aniline the elimination of 3.4% methyl chloride may be explained by the occurrence of the catalytic decomposition of chloracetic acid according to equation 1. The production of 30.2 % hydrogen chloride indicates that the glycine reaction (2) has progressed. Had all of the glycine decomposed according to equation 4, the carbon dioxide eliminated would likewise have had a value of 30.2% instead of the 19.2% actually obtained. It is not to be expected that all of the glycine formed, according to equation 2, would be decomposed according to equation 4. This is brought out by the following separately conducted experiment in which 6.10 grams of phenyl glycine were heated in the same manner as in this reaction. The evolved gases were passed over calcium chloride, and then into a weighed bulb of soda lime. The amount of carbon dioxide thus obtained was 0.2322 grams which is only 13.0% of theoretical.

It is a well known fact that phenyl glycine, instead of decomposing entirely to carbon dioxide and methyl aniline, condenses forming cyclic compounds.(6)

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In such reactions there is no elimination of carbon dioxide. It may therefore be concluded that in ratio B of reaction 1, the small amount of methyl chloride is due to the catalytic decomposition of chloracetic acid, and that the hydrogen chloride evolved accompanies formation of phenyl glycine according to equation 2.

Ratio C. Reaction 1.

In this ratio, the methyl chloride yield is increased to 8.7%, most likely through reaction 1. There is a marked increase in the yields of carbon dioxide and hydrogen chloride, 40.4% and 53.9% respectively, indicating the further progress of reactions 2 and 4, or the less extensive progress of either reaction 8 or 9.

Ratio D. Reaction 1.

In this instance it is again evident that as the quantity of chloracetic acid is increased, the yields of each of the volatile products is also increased. Each respective yield is attributed to reaction 1, 2 and 4 respectively. The high yield of hydrogen chloride, indicates that reactions 10, 11 and 12 proceed only to a limited extent. The small initial amount of amine in this reaction mixture warrants this assumption.

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Reaction II. Monomethyl Aniline and Chloracetic Acid.

All of the possible reactions, between methyl aniline and chloracetic acid, which might influence the amounts of carbon dioxide, hydrogen chloride and methyl chloride are as follows:*

1. $CH_2ClCO_2H \longrightarrow CH_3Cl + CO_2$
6. $C_6H_5NHCH_3 + ClCH_2CO_2H \longrightarrow C_6H_5NCH_3CH_2CO_2H + HCl$
7. $C_6H_5NCH_3CH_2CO_2H \longrightarrow C_6H_5N(CH_3)_2 + CO_2$
9. $C_6H_5NHCH_3 + CH_3Cl \longrightarrow C_6H_5N(CH_3)_2 + HCl \rightarrow C_6H_5N(CH_3)_2HCl$
11. $C_6H_5NHCH_3 + HCl \longrightarrow C_6H_5NHCH_3 . HCl$
12. $C_6H_5N(CH_3)_2 + HCl \longrightarrow C_6H_5N(CH_3)_2HCl$
13. $C_6H_5N(CH_3)_2 + ClCH_2CO_2H \longrightarrow C_6H_5NCH_3CH_2CO_2H + CH_3Cl$

Ratio A. Reaction II.

This ratio is characterized by an increase in the yields of both carbon dioxide and methyl chloride, over the amounts of those products obtained in the same ratio of aniline and acetic acid, (Ratio A. Reaction 1). The amount of hydrogen chloride is less than one percent of the theoretical. The increase in carbon dioxide must be due either to an increase in the extent of the catalytic reaction 1, or to a greater decomposition (reaction 7) of the methylphenylamino acetic acid which is previously formed according to reaction6.

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* Those equations which are identical with the equations postulated under Reaction 1 will be indicated by the identical numbers, and reference will be made to them accordingly. Other possible reactions will be assigned numbers consecutive to those previously indicated under reaction 1, and so on throughout the subsequent interpretations of reactions III, IV, and V.

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But it is quite logical to assume that there should be a decrease in the amount of glycine formed (equations 6) through elimination of hydrogen chloride, because there is only one available hydrogen atom in methyl aniline that is susceptable to the action of chloracetic acid. In this event carbon dioxide would occur chiefly through the catalytic decomposition reaction (1). If this is true it accounts quite well for the increased amount of methyl chloride produced. However, the increase in methyl chloride may also be explained by a reaction similar to the glycine reaction number 6, namely number 13. Granting that carbon dioxide is partly due to a decomposition of phenyl-methyl-amino-acetic acid, according to reaction number 7, the reformation of dimethyl aniline amounts to a catalytic reaction.

$$\begin{array}{lll}
\text{(Reaction 7) } C_6H_5N(CH_3)_2 + ClCH_2CO_2H & \longrightarrow & C_6H_5NCH_3CH_2CO_2H + CH_3Cl \\
\text{(Reaction 13) } C_6H_5NCH_3CH_2CO_2H & \longrightarrow & C_6H_5N(CH_3)_2 + CO_2 \\
\hline
C_6H_5N(CH_3)_2 + ClCH_2CO_2H & \longrightarrow & C_6H_5N(CH_3)_2 + CO_2 + CH_3Cl.
\end{array}$$

The small amount of hydrogen chloride evolved in this reaction may be explained by the formation of amine hydrochlorides, reactions 11 and 12.

Ratio B. Reaction II.

In this ratio there is an increase in the amounts of all three gases evolved, over the amounts formed in the

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preceding ratio. It is significant that the methyl chloride yield, 62.9%, exceeds that of carbon dioxide, 52.4%, and that hydrogen chloride increases only to 5.7%. This is in marked contrast with the fact that the increase of hydrogen chloride through ratios A and B in reaction I was 30.1%.

The large yields of both carbon dioxide and of methyl chloride indicate the preponderance of the catalytic reaction 7. The increased yield of methyl chloride over the carbon dioxide would point to reaction 13. If 13 and 7 take place simultaneously the reaction would really amount to the catalytic reaction previously noted in ratio B, reaction II.

Ratio C. Reaction II.

There is an increase in both carbon dioxide and hydrogen chloride evolution, but the methyl chloride yield is the same as in the preceding ratio B, 62.9%. The increase in the hydrogen chloride yield points to a decrease in the extend of the reaction 11 and 12, due to the decreasing ratio of amine to acid. An increase in the extent of reaction 6, which naturally precedes reaction 7 may be logically inferred. This is substantiated by the increased yield of carbon dioxide (reaction 7). The absence of any change in the yield of methyl chloride through ratios B and C leads to the assumption that reactions 1 and 13 have reached a maximum in this ratio of

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methyl aniline and chloracetic acid.

Ratio D. Reaction II.

Here again there is a further increase in the yields of carbon dioxide and hydrogen chloride but a decrease in that of methyl chloride. This decrease may be explained by reaction 9 which involves the formation of dimethyl aniline and the liberation of hydrogen chloride. The following experiment was performed to prove this assumption.

The reaction mixture (Ratio D, Reaction II) was first neutralized with a sodium carbonate solution and then extracted with ether. After removing the ether by distillation there remained a yellow oil having a boiling point of 193°C. This oil was dissolved in an excess of concentrated hydrochloric acid, cooled to 0°C and a cold solution of sodium nitrite was added. Yellow needles of the hydrochloride of para-nitrosodimethyl aniline separated on standing. This proves that dimethyl aniline was produced during the reaction between monomethyl aniline and chloracetic acid. This in conjunction with the increase in hydrogen chloride would indicate that reaction 9 had taken place.

The relative yields of carbon dioxide, 64.9%, and hydrogen chloride, 32.1%, seem to indicate that the catalytic reaction predominates over the reaction which forms

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methylphenylglycine, and, therefore, its subsequent decomposition. The small amount of methyl aniline used would not warrant the assumption that reaction 11 and 12 proceed to any appreciable extent.

It is to be concluded, generally, that as the amount of methyl aniline is decreased, in the various reaction mixtures, the extent to which the catalytic reaction I proceeds is increased.

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Reaction III. Monoethyl Aniline.

The following equations represent all of the possible reactions which might influence the production of the three gaseous products from the interaction between acetic acid and monoethyl aniline.

1. $ClCH_2CO_2H \longrightarrow CH_3Cl + CO_2$

14.$C_6H_5NHC_2H_5 + ClCH_2CO_2H \longrightarrow C_6H_5NC_2H_5CH_2CO_2H + HCl$

15.$C_6H_5NCH_3CH_2CO_2H \longrightarrow C_6H_5NC_2H_5CH_3 + CO_2$

16.$C_6H_5NCH_3C_2H_5 + ClCH_2CO_2H \longrightarrow C_6H_5NC_2H_5CH_2CO_2H + CH_3Cl$

17.$C_6H_5NCH_3C_2H_5 + ClCH_2CO_2H \longrightarrow C_6H_5NCH_3CH_2CO_2H + C_2H_5Cl$

7. $C_6H_5NCH_3CH_2CO_2H \longrightarrow C_6H_5N(CH_3)_2 + CO_2$

18.$C_6H_5NHC_2H_5 + CH_3Cl \longrightarrow C_6H_5NC_2H_5CH_3 + HCl(C_6H_5NC_2H_5CH_3.HCl)$.

19.$C_6H_5NHC_2H_5 + HCl \longrightarrow C_6H_5NHC_2H_5.HCl$

20.$C_6H_5NC_2H_5CH_3 + HCl \longrightarrow C_6H_5NC_2H_5CH_3\ .HCl$

Ratio A. Reaction III.

The percentages of carbon dioxide, 40.8%, and hydrogen chloride, 0.58%, evolved in this ratio, are practically the same as the yields in ratio A of reaction II. The alkyl chloride yield is much higher than that obtained in any of the other experiments, namely 75.0%

The hydrogen chloride must proceed from the glycine reaction 14. The very small amount of the hydrogen chloride liberated must be due to the operation of reactions 19 and 20 producing amine hydrochlorides.

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Carbon dioxide must be formed by the catalytic reaction (1), through the decomposition of phenylethylaminoacetic acid (15) or of methylphenylaminoacetic acid (7). Alkyl chloride may be the result of reactions 1, 16 or 17 singly or simultaneously. If reaction 17 does take place the substance absorbed and weighed in the charcoal must have contained ethyl - as well as methyl chloride. The following experiment was carried out with the view of determining this point, namely the simultaneous liberation of both methyl and ethyl chloride.

Ethyl aniline and chloracetic acid, in the molar ratio of 2:1, were heated together in a long neck, round bottom flask connected with a reflux condenser from which a tube extended into a long test tube surrounded by ether and carbon dioxide snow, (-70°C.) A colorless low boiling liquid condensed. This was mixed with concentrated sodium hydroxide solution and heated in a sealed tube at 120°C for several hours in order to convert methyl and ethyl chloride into their corresponding alcohols. The reaction product was then placed in a distilling flask connected with a condenser and heated in a water bath. The distillate was tested for methyl and ethyl alcohol as follows.

A few drops of the distillate were diluted with

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5 cc. water. A hot copper wire was then repeatedly plunged into the solution to insure oxidation of alcohol to aldehyde. A few drops of resorcin was then added to 1 cc. of the solution and concentrated sulphuric introduced as a lower layer. A red ring at the junction of the two liquids indicated the presence of formaldehyde.

A few drops of an alcoholic solution of gallic acid were added to another portion of the liquid. Introduction of concentrated sulphuric acid as a lower layer caused the formation of a blue ring. This confirmed the presence of formaldehyde.

A portion of the distillate was tested for ethyl alcohol. The solution was made alkaline with sodium hydroxide and a few crystals of iodine added. On heating this solution iodoform was produced, confirming the presence of ethyl alcohol. This proves conclusively that ethyl chloride was evolved. Reaction 17 affords an explanation.

The data for alkyl chloride therefore represents a mixture of methyl and ethyl chlorides, but it is calculated from the amount of methyl chloride which a given amount of chloracetic acid would yield through the catalytic reaction I. It was not feasible in this thesis to undertake the development of methods which would enable one to estimate the respective yields of methyl chloride and ethyl chloride.

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Ratio B. Reaction III.

In proceeding from ratio A to ratio B an increase in the amounts of all three gases is noticed. It is significant that the increase in the yield of hydrogen chloride is quite small, namely from 0.58% to 2.8%. The increase in hydrogen chloride output, through the same ratios in reaction I (aniline) is from 0.04% to 30.2%. Apparently the substitution of an amino hydrogen for an ethyl radical inhibits the production of hydrogen chloride. The hydrogen chloride is produced through the glycine reaction (14) and possibly reaction (18). The amounts of hydrogen chloride produced must be an approximate index, of the extent of the glycine reaction (14), especially since the initial amount of the amine used does not warrant the assumption that reactions 19 and 20 proceed to any great extent.

Carbon dioxide is formed through reactions 1, 15 and 7. A repetition of the experiment described in the preceding section using equimolar quantities of amine and acid reveals the fact that ethyl chloride is also produced in the reaction. Therefore alkyl chloride must be the result of reactions 1, 16 and 17.

Ratio C Reaction III.

This ratio is characterized by a further increase in the amounts of carbon dioxide and hydrogen chloride and by a slight decrease in the amount of alkyl chloride formed.

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Carbon dioxide is produced by reaction 1, 15 and 7. The presence of ethyl chloride in the gas mixture warrants the assumption that reaction 17 does take place. The decrease in the amount of alkyl chloride is to be expected to accompany a decrease in the initial amount of ethyl-aniline used. As the concentration of ethyl aniline is decreased through the various ratios the extent to which reaction 17 proceeds, should also be expected to decrease, with a consequent decrease in the amount of ethyl chloride formed.

Ratio D. Reaction III.

There is a further increase in the carbon dioxide and hydrogen chloride yields and a decrease in the alkyl chloride yields. Carbon dioxide and hydrogen chloride are the result of reactions 1, 14, 18 and perhaps, to a slight measure, reaction 7. The very small initial amount of amine used in this experiment does not warrant the assumption that reaction 17 has taken place to as great an extent as previously, so that ethyl chloride evolution is decreased.

The small concentration of amine in the reaction mixture prevents the formation of amine hydrochlorides according to reactions 19 and 20.

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Reaction IV. Dimethyl Aniline and Chloracetic Acid.

The seven equations which follow represent all of the possible reactions between dimethyl aniline and chloracetic acid which may influence the evolution of carbon dioxide, hydrogen chloride and alkyl chloride.

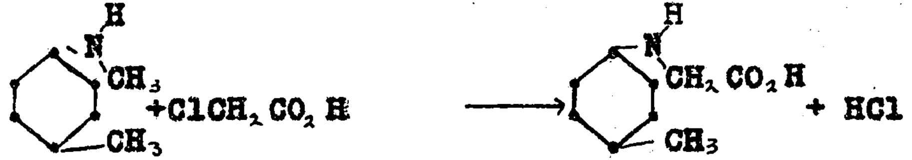
1. $CH_2ClCO_2H \longrightarrow CH_3Cl + CO_2$

21. $C_6H_5N(CH_3)_2 + CH_2ClCO_2H \longrightarrow C_6H_5NCH_3CH_2CO_2H + CH_3Cl$

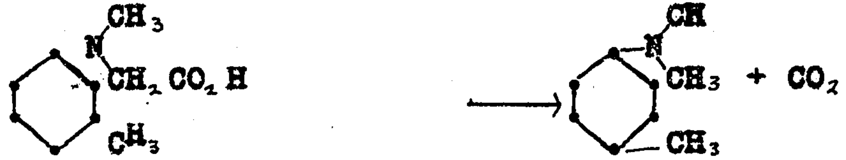
7. $C_6H_5NCH_3CH_2CO_2H \longrightarrow C_6H_5N(CH_3)_2 + CO_2$

22.

23.



24.



12. $C_6H_5N(CH_3)_2 + HCl \longrightarrow C_6H_5N(CH_3)_2 \cdot HCl.$

Ratio A. Reaction IV.

The yields of carbon dioxide and hydrogen chloride are 22.1% and 0.4% respectively. The value for carbon dioxide is lower than that in the same ratio with mono-methyl aniline. On the other hand the yield of methyl chloride is very high, 92.0%. The source of carbon dioxide may be attributed to reactions 1,7 and 24;

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the methyl chloride, to reactions 1 and 21.

With dimethyl aniline the elimination of hydrogen chloride would be expected to take place only to a limited degree and would be made possible only through the well known para-rearrangement reaction, which substitutes hydrogen for the alkyl of the amino group. This reaction is represented by equation 22. It is highly improbable that there should be substitution of any of the hydrogen atoms of the nucleus to form hydrogen chloride. Such reactions are unknown. If, in this ratio, the para-rearrangement does take place, then reaction 24 may follow and the hydrogen chloride thus formed would be held back, according to reaction 12, due to the excess of the amine in this reaction mixture of 2 moles amine to 1 mole acid.

Ratio B. Reaction IV.

In proceeding from ratio A to ratio B, there is an increase in the yields of carbon dioxide and methyl chloride, but practically no hydrogen chloride is evolved. Carbon dioxide must again be assumed to proceed from reaction 1, 7 and 24. If reaction 1 were the sole source of methyl chloride and carbon dioxide, then the methyl chloride yield should equal that of carbon dioxide. Since, however, the methyl chloride yield (94.4%) is much

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greater than that of carbon dioxide (36.8%), then reaction 21 must be assumed to have been the source of excess methyl chloride. No increase in the amount of hydrogen chloride evolved in this ratio, and the comparatively small initial amount of amine used, do not warrant the assumption that reaction 23 has taken place to any appreciable extent.

Ratio C. Reaction IV.

The yield of carbon dioxide (51.7%) continues to increase through this ratio, while the hydrogen chloride yield only advances to 2.4%. The methyl chloride has reached a maximum yield in the previous ratio (94.4%) and now slightly decreases to 92.9%. Carbon dioxide again may be assumed to have been formed through reactions 1, 7 and 24. The yield of 2.4% hydrogen chloride must result from the glycine reaction 23. The small initial amount of amine does not warrant the assumption that equation 12 has taken place to any great extent, so that, in this ratio, the amount of hydrogen chloride evolved may be a fair measure of the extent of the para-rearrangement. The very slight decrease in the methyl chloride yield must point to a slight decrease in the extent to which reaction 21 takes place, due, in turn to a small concentration of amine in the reaction mixture.

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Ratio D. Reaction IV.

There is a further increase in the yields of carbon dioxide and hydrogen chloride but a decrease in that of methyl chloride. Carbon dioxide proceeds from reactions 1, 7 and possibly 24. The greatly increased yield of hydrogen chloride (23.1%) indicates that reaction 23 has taken place and this lends weight to the assumption that part of the carbon dioxide proceeds from the decomposition reaction 24.

The small initial amount of dimethyl aniline used would not lend itself to any extensive retention of hydrogen chloride according to equation 12.

Methyl chloride proceeds from the catalytic reaction (1), or the glycine reaction (21) which results in the formation of methylphenylaminoacetic acid. The diminution in methyl chloride yield is explained by the decrease in reaction 21, which would follow a decrease in the amount of dimethyl aniline used in the reaction mixture.

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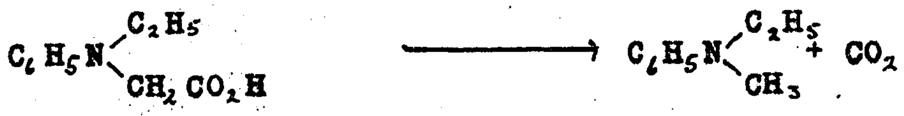
Reaction V. Diethyl Aniline.

All of the reactions which may effect the elimination of carbon dioxide, hydrogen chloride or alkyl chloride from the interaction of chloracetic acid and diethyl aniline are represented by the following equations.

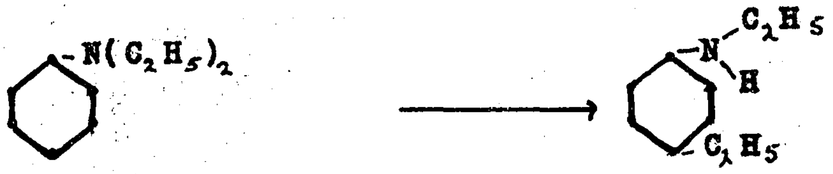
1. $CH_2ClCO_2H \longrightarrow CH_3Cl + CO_2$

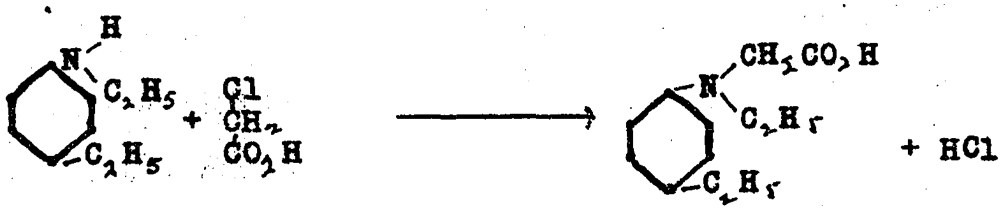
25.

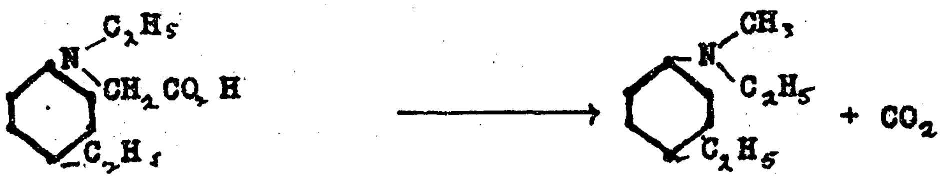

$C_6H_5N(C_2H_5)_2 + \overset{Cl}{\underset{CO_2H}{CH_2}} \longrightarrow C_6H_5N\begin{matrix} C_2H_5 \\ CH_3 \end{matrix} + CO_2$

15.


$C_6H_5N\begin{matrix} C_2H_5 \\ CH_2CO_2H \end{matrix} \longrightarrow C_6H_5N\begin{matrix} C_2H_5 \\ CH_3 \end{matrix} + CO_2$

26.


27.


28.


29. $C_6H_5N(C_2H_5)_2 + HCl \longrightarrow C_6H_5N(C_2H_5)_2 \cdot HCl$

30. $C_6H_5NC_2H_5CH_3 + HCl \longrightarrow C_6H_5NCH_3C_2H_5 \cdot HCl.$

Ratio A. Reaction V.

The yields of carbon dioxide and hydrogen chlor-

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ide are small, namely 11.4% and 0.1% respectively. It is interesting to note that the yields of carbon dioxide is smaller than that from any of the other reactions. The carbon dioxide may proceed from the catalytic reaction 1 and from the decomposition reaction 28. If carbon dioxide proceeds from reaction 28, then it would have been preceded by reaction 27. The extent of reaction 27 would be indicated by the amount of hydrogen chloride produced. Although hydrogen chloride would be held back by reaction 29 and 30, i.e., through the excess of amine present in this ratio, this retention would be less in the next ratio, B. But there is no increase in the hydrogen chloride output in ratio B over ratio A. The absence of increase in B, naturally leads to the assumption that little hydrogen chloride was formed in A. It would then follow that little para-ethylphenylethylaminoacetic acid was formed. This being the case, the major part of the carbon dioxide must proceed from reaction 1 and not from reaction 28.

In this reaction the substance absorbed in the charcoal was a mixture of both ethyl and methyl chlorides. Accordingly the data for alkyl chloride represents a mixture of methyl and ethyl chlorides and is calculated from the amount of methyl chloride which chloracetic acid would have given if it had entirely decomposed

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according to the catalytic reaction 1. Methyl chloride must have been produced through the reaction represented by equation 1; ethyl chloride, by reaction 25. The large excess of di-ethyl aniline would naturally have increased the extent to which reaction 25 took place. The presence of ethyl chloride, explains on the basis of the calculated yield of methyl chloride, the fact that the yield is greater than 100%. This also is true in reaction mixtures B and C.

Ratio B. Reaction V.

There is here a still further increase in the amount of carbon dioxide evolved but the yield of hydrogen chloride remains practically the same in the preceding ratio A. There is a negligible decrease, 0.7%, in the amount of alkyl chloride eliminated.

The small amount of hydrogen chloride evolved in this ratio together with the small amount of amine used would not warrant the assumption that the para-rearrangement (26), or the glycine reaction (27) had occurred to any great extent. Consequently, reaction 28 cannot be the source of any great amount of carbon dioxide. The principal amount of carbon dioxide then must be through glycine reaction 1.

The alkyl chloride, really a mixture of methyl

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and ethyl chlorides, is the result of the catalytic reaction 1, and the glycine reaction 25.

Ratio C. Reaction V.

A decrease in the amount of alkyl chloride evolved is noted in this ratio. There is an increase in both carbon dioxide and hydrogen chloride. The increase in the hydrogen chloride yield indicates presumably, an increase in the extent of reactions 26 and 27. Therefore, a part of the carbon dioxide must find its source in reaction 28. Carbon dioxide is also formed together with methyl chloride, through reaction 1. The decrease in alkyl chlorides, which accompanies the decrease in the amount of amine used, must be due to a further decrease in reaction 25, which eliminates ethyl chloride of greater molecular weight than methyl chloride.

Ratio D. Reaction V.

The carbon dioxide and hydrogen chloride yields increase in this ratio, especially the latter. There is a large decrease in alkyl chlorides through ratios C and D, namely from 104.9% to 66.8%.

The large yield of hydrogen chloride (26.6%) indicates a material increase in the extent to which reactions 26 and 27 take place. Reactions 29 and 30, which represent the formation of amine hydrochlorides

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most likely takes place only to a very slight extent because of the small amount of dimethyl aniline used in the reaction mixtures. Hence, there is little or no interference with the elimination of free hydrogen chloride.

Since reaction 27 takes place, (as indicated by the hydrogen chloride evolved), carbon dioxide must also be formed by the catalytic reaction 1.

Methyl chloride is formed through equation 1, the catalytic decomposition, ethyl chloride is due to reaction 25. The small concentration of diethyl aniline must inhibit the formation of ethyl chloride through equation 25, so that the total amount of alkyl chloride should be expected to decrease in this ratio. The data confirms this prediction

The Catalytic Decomposition Reaction.

A survey of the various reactions proposed to account for the production of the three gaseous products, reveals the fact that the production of carbon dioxide and methyl chloride is, in each case, partly due to the catalytic decomposition of chloracetic acid. Other cases of similar decomposition, previously announced by Hemmelymayr, Cazeneuve, and Fry, have been noted in the historical section.

Fry(7) has explained the instability of carboxyl

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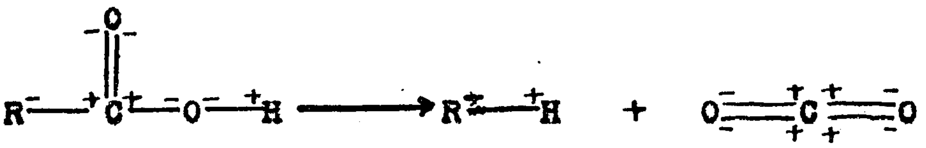
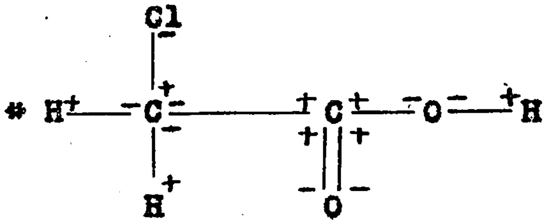
groups by his theory of positive and negative valences. He states that when the carbon atom of a carboxyl group bears four positive charges, then and only then is the elimination of carbon dioxide possible. Such carboxyls are always unstable and yield carbon dioxide on decomposition. This is expressed by the following electronic equation:



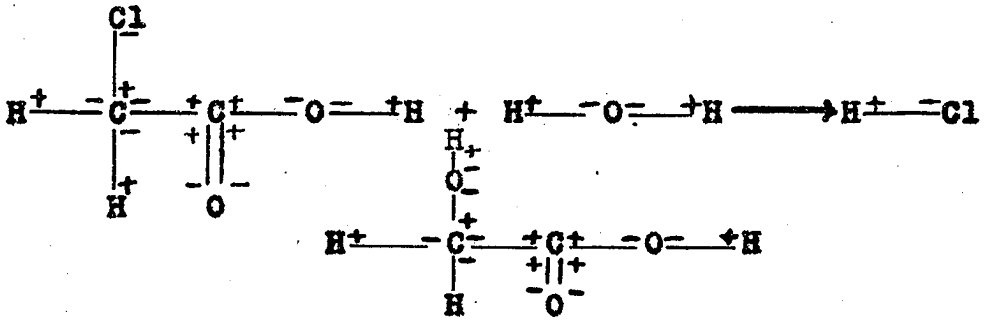
$$R^{-}\!-\!{}^{+}\overset{\overset{-O-}{\|}}{C}{}^{+}\!-\!{}^{-}O^{-}\!-\!{}^{+}H \longrightarrow R^{\pm}\!-\!{}^{+}H + O\overset{-\,+}{\underset{-\,+}{=}}C\overset{+\,-}{\underset{+\,-}{=}}O$$

The preparation of acetic acid by Wanklyn through the interaction of sodium methylate and carbon dioxide, warrants the assumption that the valences of the carboxyl carbon atom, in the acetic acid molecule and in its derivatives, are entirely positive. The electronic formula of chloracetic acid would then be:



$$* \; H^{+}\!-\!{}^{-}\underset{\underset{H^{+}}{|^{-}}}{\overset{\overset{Cl}{|^{-}}}{C^{+}}}{}^{-}\!-\!{}^{+}\underset{\underset{-O-}{+\|+}}{C}{}^{+}\!-\!{}^{-}O^{-}\!-\!{}^{+}H$$

* Since hydrolysis gives glycollic acid, the chlorine atom, under these conditions, is presumably negative.



$$H^{+}\!-\!{}^{-}\underset{\underset{H^{+}}{|^{-}}}{\overset{\overset{Cl}{|^{-}}}{C^{+}}}{}^{-}\!-\!{}^{+}\underset{\underset{-O-}{+\|+}}{C}{}^{+}\!-\!{}^{-}O^{-}\!-\!{}^{+}H + H^{+}\!-\!{}^{-}O^{-}\!-\!{}^{+}H \longrightarrow H^{+}\!-\!{}^{-}Cl$$

$$H^{+}\!-\!{}^{-}\underset{\underset{H}{|^{-}}}{\overset{\overset{\overset{H_{+}}{O^{-}}}{|^{+}}}{C^{-}}}\!-\!{}^{+}\underset{\underset{-O-}{+\|+}}{C}{}^{+}\!-\!{}^{-}O^{-}\!-\!{}^{+}H$$

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It is not surprising, then, that chloracetic acid decomposes according to the equation:

$$ClCH_2CO_2H \longrightarrow CH_3Cl + CO_2.$$

General Conclusions.

The foregoing data for the various yields of gaseous products obtained from the five reactions investigated are indicated in the following graphs, I to V. A number of the general tendencies noted in the prededing interpretations are thus more apparent.

1. In each of the five reactions, the yields of carbon dioxide and hydrogen chloride increase successively through the ratios A, B, C and D.

2. In reaction 1, the yields of alkyl chloride increase as the ratio of amine to acid is decreased.

3. In reactions II, III and IV, alkyl chloride increases through ratios A and B and decreases in ratios C and D.

4. There is a steady decrease in the yield of alkyl chloride in reaction V.

5. In proceeding from the primary amines to the tertiary amines there is a decrease in the yield of hydrogen chloride.

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Summary.

1. Experimental methods have been developed to determine quantitatively the yields of the several gases produced when chloracetic acid is heated with various amines. An entirely new method has been devised for the quantitative estimation of methyl chloride in mixtures of carbon dioxide and hydrogen chloride. Methods for the quantitative estimation of carbon dioxide and hydrogen chloride have also been developed and described.

2. All of the reactions which may have influenced the production of the three gases have been considered.

3. The possible function of each of these reactions in determining the various yields of the gases produced, have been taken into account in the proposed interpretations of the data.

4. The great number of chemical changes occurring in each reaction mixture, and the variety of non-volatile products formed, making it impossible in the scope of this thesis to investigate the residues of each of the twenty reaction mixtures. A complete quantitative study of a single reaction mixture would supply sufficient material for a thesis in itself.

5. The quantitative estimation of the gaseous products developed and described in this thesis, supplies a point of view for the investigation of any subsequent

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work which may be undertaken in a quantitative study of the interaction of monochlor, and other chloracetic acids, upon aniline or any other aromatic amine, primary, secondary or tertiary.

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