TERTIARY AMMONIUM CHLORIDES
A PROBLEM IN ORGANIC QUALITATIVE ANALYSIS

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CHAPTER I

STATEMENT OF THE PROBLEM

In organic qualitative analysis, identification of different organic compounds is accomplished by meticulous preparation of various derivatives. Each derivative should be easily and quickly made and is usually a solid because the solid is easier to isolate and purify in small amounts. The melting point of a solid is more accurate and easier to determine than is the boiling point of a liquid.

In the usual organic qualitative analysis course, tertiary amines are identified by conversion to a solid salt. The usual derivatives of tertiary amines are the quaternary ammonium salts formed by the reaction of the amine with methyl iodide, methyl-p-toluenesulfonate, or benzyl chloride. The salts of halogen acids, picric acid, or chloroplatinic may also be employed as derivatives.[1] Unfortunately not all tertiary amines respond favorably to reactions with the various types of derivatives to produce a reliable product with an accurate melting point. A student is frequently required to prepare a number of salts before a single sharp melting derivative can be obtained.

We were especially interested in the reaction between a tertiary amine and hydrogen chloride because a simple salt results from the direct union of the amine and the gaseous substance. The observed melting point for some tertiary amine hydrochlorides varies. For example, N-N dimethylaniline hydrochloride reportedly melts at 70-75°C [2] and 85-95°C [3]. In this study an attempt was made to define the factors causing inconsistent melting points and problems complicating the preparation of pure amine hydrochlorides.

CHAPTER II

REVIEW OF THE LITERATURE

In organic qualitative analysis, we are interested in obtaining the purest possible derivative for an accurate melting point. It is important to use the purest tertiary amine and hydrogen chloride available in order to obtain a pure salt. Hydrogen chloride gas is commonly produced by adding concentrated sulfuric acid to dry sodium chloride and is then directly passed into an amine solution in ether. The resulting salts are insoluble in this solvent and precipitate quantitatively.[4] Purification is not commonly attempted with amine salts because pure crystalline products supposedly are formed and recrystallization of hydrochloride salts is usually difficult. If impurities are present in the amine hydrochloride they will produce variations in the melting point.

It has been cited in the literature that melting points of the hydrobromide and hydrochloride salts of tertiary amines are not particularly suitable since these salts melt with decomposition at temperatures that are often dependent on the rate of heating.[5] A number of amine hydrochlorides may be obtained by passing dry hydrogen chloride into an ether solution of the amine.[6] If the hydrogen chloride gas is not properly dried, the gas could contain some water vapor which could combine with the amine hydrochloride as a hydrate and lead to errors or discrepancies in the melting point. Old literature references suggest drying the hydrogen chloride gas by passing it through either a concentrated sulfuric acid bath or anhydrous calcium chloride.

The production of hydrogen chloride gas was obtained by the addition of concentrated sulfuric acid to sodium chloride. The gas was bubbled into an ether solution containing a 5 to 10% solution of the amine. This method was employed by a group of students in a freshmen chemistry class at this university. The following equation describes the procedure:

$$H_2SO_{4(conc)} + NaCl_{(s)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)} \uparrow$$

$$R_3N{:}_{(l)} + HCl \longrightarrow R_3N\text{-}HCl_{(s)} .$$

This method was found to be undersirable because a poor tertiary amine hydrochloride derivative was produced. The students found discrepancies as large as 20°C between their melting points and recorded literature values. The hydrogen chloride gas was then dried by passing its vapors through anhydrous calcium chloride. The students still failed to prepare a tertiary amine hydrochloride derivative with an accurate melting point.

For each amine all the students used identical starting materials from the same reagent bottles, yet the observed melting points ranged both above and below melting points recorded in the literature. Twelve students were originally involved in the special project of the analysis of amine salts. They found variations in their melting points which ranged approximately 10°C from the average value. The student variations in melting points of amine hydrochlorides are listed in Table I.

It was originally proposed that the amines must contain impurities or be isolated in various hydrated forms. This led Mr. John Storlie and Mr. James Olson of this department to investigate the discrepancies in the tertiary amine hydrochloride melting points. They investigated the possible hydrate formation of 2-picoline hydrochloride since its melting point disagreed about 5°C with the accepted value. The 2-picoline hydrochloride was produced by bubbling freshly generated dried hydrogen chloride gas through a 5% solution of reagent grade 2-picoline in anhydrous ethyl ether. The 2-picoline hydrochloride was dried for 48 hours in a vacuum dessicator at 10 torr.

As established by aqueous titration with sodium hydroxide to a phenolphthalein end point, average purity of 2-picoline hydrochloride was 99.83% before melting and 99.75% after melting with a standard deviation of 0.08%. Ultraviolet absorption spectra were run on samples of 2-picoline hydrochloride with a Beckman Model DB spectrophotometer at a concentration of 7 mg./100 ml. of ethanol before and after melting. Molar extinction coefficients were identical within experimental error. They could not determine or locate any impurities which might have explained the discrepancies in its melting point. This procedure appeared to provide no

TABLE I

STUDENT AVERAGE VALUES FOR MELTING POINTS OF AMINE HYDROCHLORIDES

Compound	Experimental Range °C	Experimental Values °C	Literature Values °C
Tribenzylamine Hydrochloride	231-237°C	234 °C	227-228°C (7)
2-Picoline Hydrochloride	74- 77	75.5	80 (8)
N-N Dimethylaniline Hydrochloride	97-120	111	70- 75 (9) 85- 95 (10)
N-N Diethylaniline Hydrochloride	148-154	151	158 (11)

experimental explanation for the variation in the melting point.

The possibility of a hydrate formation does exist for some tertiary amine hydrochlorides; for example, pyridine and quinoline hydrochlorides are very hydroscopic. This could explain discrepancies in the observed melting points of some tertiary amine hydrochlorides.

It was observed that the student could repeat the experiment under identical conditions, by bubbling the dried hydrogen chloride into the particular amine solution and still obtain variation in the hydrochloride melting point. This would indicate that the melting point of amine hydrochlorides are dependent upon the individual technique employed by a student. A new melting point was obtained each time N-N dimethylaniline hydrochloride was produced. This would indicate that the rate of hydrogen chloride production could lead to some variation in the melting point of tertiary amine hydrochlorides. The students also observed that successive melting points often varied when a given sample was melted repeatedly. This would indicate either decomposition or volatilization of some impurity contained in the hydrochloride derivative.

We concluded the possibility that some impurities other than hydrates, must exist in the amine hydrochloride salts to explain the variations in melting points. If the tertiary amine hydrochloride salts contain impurities, they might originate in either the sodium chloride or sulfuric acid. The sodium chloride could contain some carbonate impurity which could be released by the addition of sulfuric acid. The sulfuric acid could react with the carbonate, producing carbon dioxide gas, which could possibly react with the tertiary amine. The likelihood of any carbonate impurities is small because carbonate salts are unstable under the acid conditions found in the amine solution. The only other possibility is that the sulfuric acid must decompose when it reacts with the sodium chloride. The equilibrium between sulfuric acid and water and sulfur trioxide is well known in the contact process for sulfuric acid:

$$H_2O_{(l)} + SO_3 \rightleftharpoons H_2SO_{4(l)} .$$

The reaction as written is extremely exothermic. Hydrogen chloride is released from the sodium chloride and sulfuric acid in an exothermic reaction which could lead to local hot spots and possibly generate sulfur trioxide.

$$H_2SO_{4(l)} + NaCl_{(s)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

$$H_2SO_{4(l)} \rightleftharpoons H_2O_{(l)} + SO_3$$

If sulfur trioxide were produced by some hot spots within the sodium chloride, then a tertiary amine sulfonate could result. Sulfur trioxide is known to produce a highly polar, salt-like amine sulfonate on reaction with tertiary amines:[12]

$$R_3N:_{(l)} \quad + \quad SO_3 \longrightarrow R_3N\text{-}SO_{3(s)} \,.$$

If a mixture of a tertiary amine hydrochloride and a tertiary amine sulfonate did result, it would explain the variation in the melting point for the salt. A small amount of the amine sulfonate would not greatly affect titer on analysis. (See page 5.)

CHAPTER III

RESULTS AND CONCLUSIONS

The technique employed to identify the sulfur trioxide was to use a saturated solution of barium chloride and to pass the hydrogen chloride into the solution. If sulfur trioxide were present an insoluble precipitate of barium sulfate would result. The barium chloride test proved conclusively that a slight amount of sulfur trioxide was generated by the reaction of concentrated sulfuric acid upon sodium chloride.

$$BaCl_{2(s)} + H_2O_{(l)} + SO_3 \longrightarrow BaSO_{4(s)}\downarrow + 2HCl_{(l)}$$

It was determined that rapid addition of sulfuric acid to dry sodium chloride without drying the hydrogen chloride vapors would immediately result in a chemical reaction between the vapors and the saturated barium chloride solution. It was observed that a white insoluble precipitate would immediately appear as the hydrogen chloride was passed into the barium chloride solution. The precipitate was identified as barium sulfate. It must be concluded that some of the concentrated sulfuric acid decomposes into water and sulfur trioxide upon addition to dry sodium chloride. Slow or rapid addition of concentrated sulfuric acid to dry sodium chloride would result in various amounts of sulfur trioxide as detected by the presence of different amounts of barium sulfate precipitate.

We proceeded to see what effect the untreated hydrogen chloride would have on the amine solution in ether. We employed the rapid addition of concentrated sulfuric acid upon dried sodium chloride and passing the hydrogen chloride directly into a 10% solution of the amine in ether. The resulting mixtures of amine hydrochlorides, amine sulfonate, and hydrates gave very unreliable melting points. The melting point of triethylamine hydrochloride varied from 225°C to 240°C which is approximately 30°C from the reported literature value of 254-255°C.[13] Melting points of other mixtures of amine sulfonates and hydrochlorides that were prepared by the rapid addition of sulfuric acid to sodium chloride and the passing of undried hydrogen chloride gas are given in Table II.

It was discovered that by heating the mixture of sodium chloride and sulfuric acid, the observed reaction rate increased, resulting in a larger amount of barium sulfate precipitate. Heating would serve to shift the equilibrium between sulfur trioxide, water and sulfuric acid toward a greater amount of sulfur trioxide. Figure I, page 13, describes the approximate relationship that exists between temperature and sulfur trioxide production. The graph was obtained by quantitative observation on the amount of barium sulfate precipitate formed from the reaction of sulfur trioxide and barium chloride. The concentrated sulfuric acid was rapidly added at room temperature to the sodium chloride for a period of five minutes. Approximately one cm. of barium sulfate precipitate was formed in

TABLE II

MELTING POINTS OF IMPURE AMINE HYDROCHLORIDES, PREPARED BY DIRECT ADDITION OF HYDROGEN CHLORIDE

Compound	Observed Value °C	Literature Value °C	
Pyridine Hydrochloride	Hygroscopic	144.5°C	(14)
Quinoline Hydrochloride	Hygroscopic	94	(15)
N-N Dimethylaniline Hydrochloride	Oil	85- 95	(16)
N-N Diethylaniline Hydrochloride	120-130°C	158	(17)
Tributylamine Hydrochloride	230-240	256-257	(18)
Tribenzylamine Hydrochloride	200-210	227-228	(19)

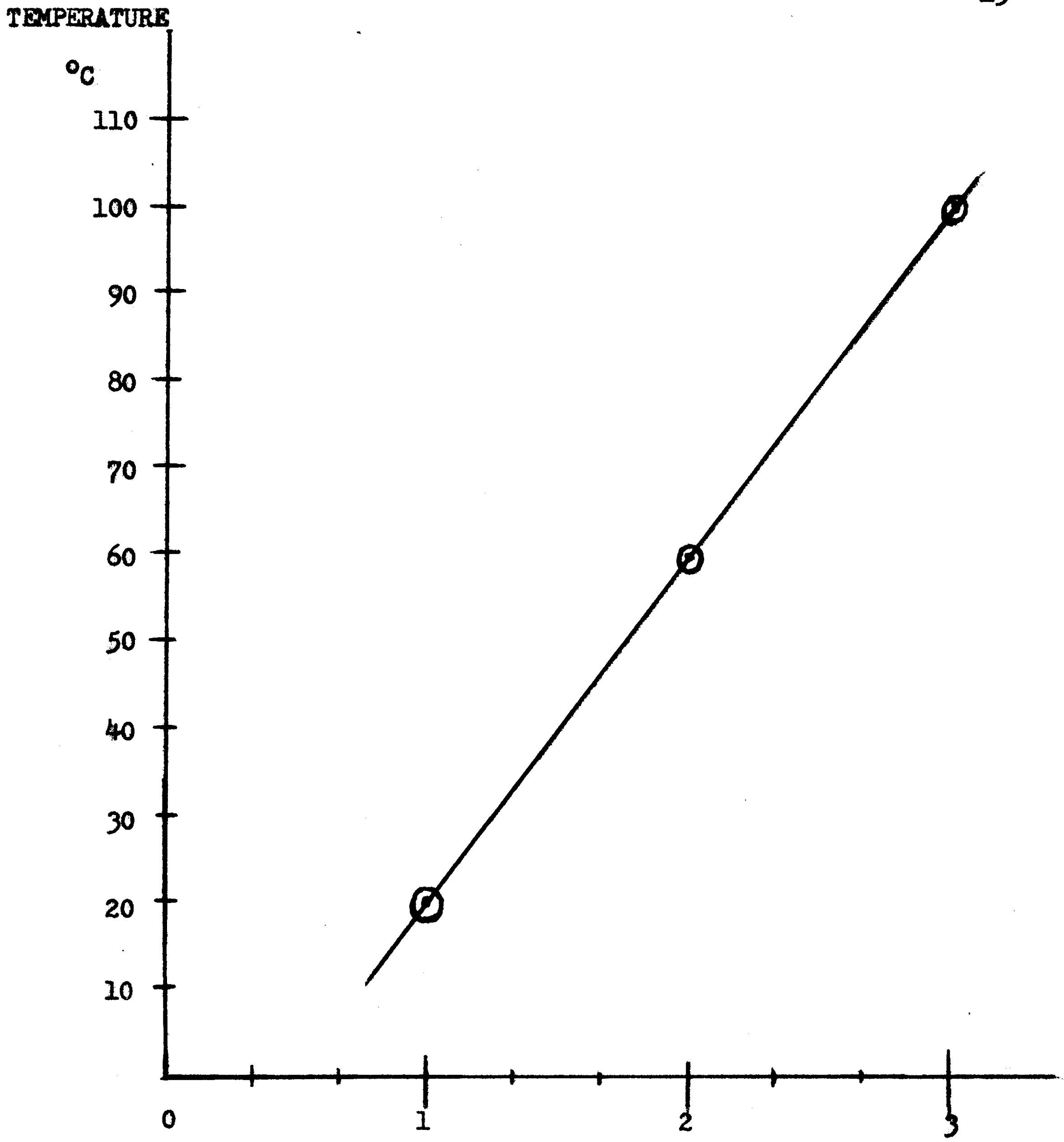


FIGURE 1

TEMPERATURE DEPENDENCE AND AMOUNT OF BARIUM SULFATE PRECIPITATED the flask used. The identical procedure was repeated except the mixture of sulfuric acid and sodium chloride was heated at 60°C for five minutes. The barium sulfate precipitate increased approximately to 2 cm. The rapid addition of sulfuric acid was repeated again but the mixture of sulfuric acid and sodium chloride was heated at 100°C for five minutes. The barium sulfate increased again approximately to 3 cm. The barium sulfate precipitate steadily increased as the temperature was raised. Therefore the amount of barium sulfate formed must be related to the amount of sulfur trioxide generated.

The following are suggestions that were employed to prevent the production of sulfur trioxide in the preparation of amine hydrochloride derivatives. As described in the chemical literature "drying or scrubbing" gaseous hydrogen chloride with concentrated sulfuric acid or anhydrous calcium chloride will remove most impurities.

It was discovered that scrubbing the hydrogen chloride gas with a single gas washer filled with concentrated sulfuric acid was ineffective because on testing a slight precipitate of barium sulfate was formed. It was observed that rapid addition of sulfuric acid to sodium chloride and passing the hydrogen chloride gas through a single gas washer produced various amounts of barium sulfate when tested with barium chloride. Even slow addition of sulfuric acid to sodium chloride produced a very slight amount of barium sulfate when tested with barium chloride.

The procedure of scrubbing hydrogen chloride with anhyrous calcium chloride was found to be less effective in eliminating sulfur trioxide than the method of using a single gas washer.

We prepared some impure amine hydrochlorides by passing the hydrogen chloride gas through a single gas washer. The sulfuric acid was added very rapidly to the sodium chloride causing the flow of a large amount of hydrogen chloride gas through the gas washer into the amine solution. This resulted in some impure amine hydrochloride derivatives contaminated by sulfur trioxide as described in Table III. This contamination could account for the differences in the melting point of various amine hydrochlorides that were prepared by the students in the freshmen class.

It was observed that the depth of the sulfuric acid scrubber was an important factor. If only 3 cm. or 4 cm. of concentrated sulfuric acid was placed in the gas washer a larger amount of barium sulfate was produced than when a depth of 15 cm. of sulfuric acid was used. Therefore the most effective cleanser of hydrogen chloride gas is a deep gas scrubber filled with at least 15 cm. of concentrated sulfuric acid, providing that the addition of sulfuric acid to sodium chloride is done carefully and slowly. For the greatest reduction in sulfur trioxide, two scrubbers in tandom filled with concentrated sulfuric acid were preferred

TABLE III

MELTING POINTS OF IMPURE AMINE HYDROCHLORIDES, PREPARED BY A SINGLE GAS WASHER

Compound	Observed Value °C	Literature Value °C
Triethylamine Hydrochloride	248-250°C	254-255°C (20)
Tributylamine Hydrochloride	251-253	256-257 (21)
Tribenzylamine Hydrochloride	220-223	227-228 (22)
N-N Diethylaniline Hydrochloride	150-155	158 (23)

to a single unit.

Another observation of the concentration of sulfuric acid that can react with sodium chloride was made. If the concentration of sulfuric acid was varied to a more dilute solution this helped to prevent sulfur trioxide production. It was found that the greatest reduction of sulfur trioxide was attained with use of 30 N sulfuric acid instead of concentrated sulfuric acid.

The best technique that was utilized for the production of pure hydrogen chloride was to slowly add 30 N sulfuric acid to reagent grade sodium chloride. This reaction produced hydrogen chloride gas which was then passed through two 15 cm. deep sulfuric acid scrubbers to remove water and sulfur trioxide. The product was tested for the presence of sulfur trioxide by passing the hydrogen chloride vapors through a barium chloride solution. No precipitate of barium sulfate was formed indicating that the hydrogen chloride must be free of sulfur trioxide.

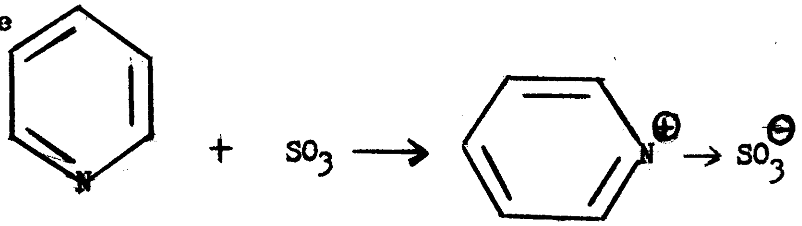
Another technique used to generate hydrogen chloride gas was to mix concentrated sulfuric acid very slowly with concentrated hydrochloric acid. This method had to be done very carefully because the concentrated sulfuric acid generated a great deal of heat on dilution with concentrated hydrochloric acid. The heat evolved, drove the equilibrium between sulfuric acid and sulfur trioxide and water toward more production of sulfur trioxide. Testing with barium chloride solution revealed that the gas generated contained more sulfur trioxide than when the hydrogen chloride gas was generated from sodium chloride.

To prevent the possibility of any sulfur trioxide impurities, it is best to use a commercial gas bottle filled with hydrogen chloride gas. When the hydrogen chloride gas is passed into the amine solution no sulfur trioxide contamination will occur.

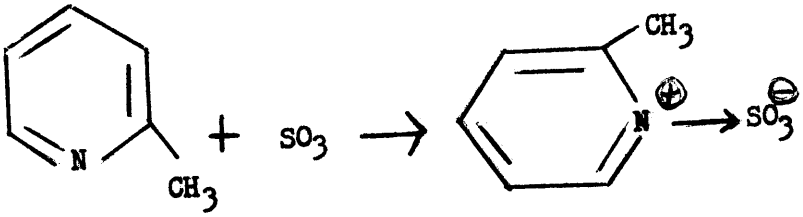
We proceeded to prove the formation of tertiary amine sulfonates under experimental conditions. The method used to produce a tertiary amine sulfonate was to heat fuming sulfuric acid to release sulfur trioxide which could react with a 10% solution of tertiary amine in an ether solution. The result in most cases attempted was the formation of an insoluble tertiary amine sulfonate salt. The amine sulfonates are crystalline solids having low solubility in benzene or ether. They have typically higher melting points than the corresponding amine hydrochlorides which might account for the melting point deviations both above and below the values recorded by others.

A series of amine sulfonates were prepared as in the manner previously cited. The following chemical reactions describe the various tertiary amines that were used to identify the presence of tertiary amine sulfonates. The melting points of amine sulfonates within experimental error are given in Table IV, page 23.

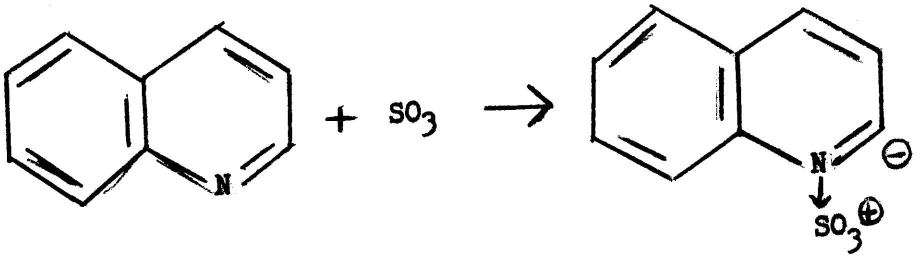
Pyridine



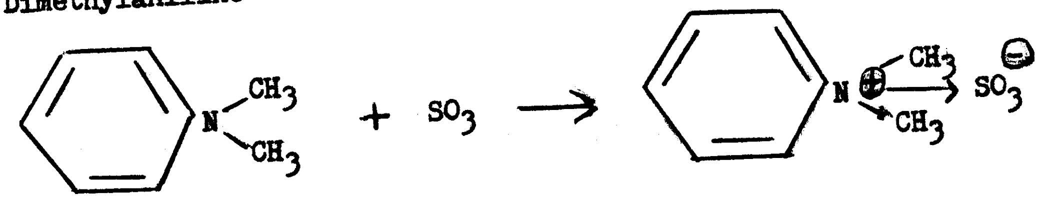
2-Picoline



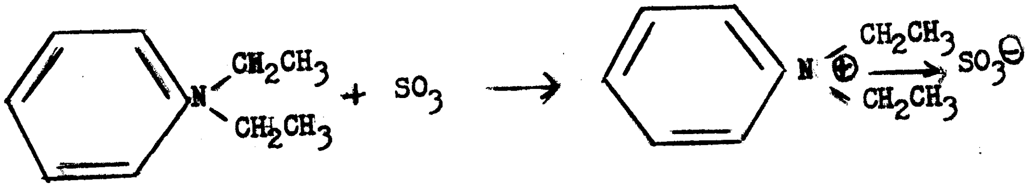
Quinoline



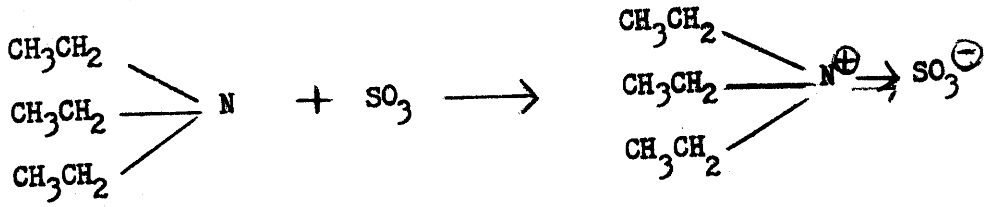
N-N Dimethylaniline



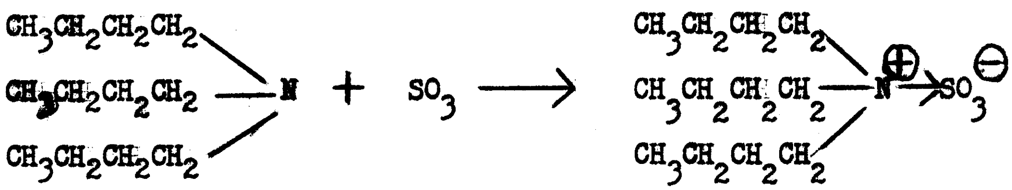
N-N Diethylaniline



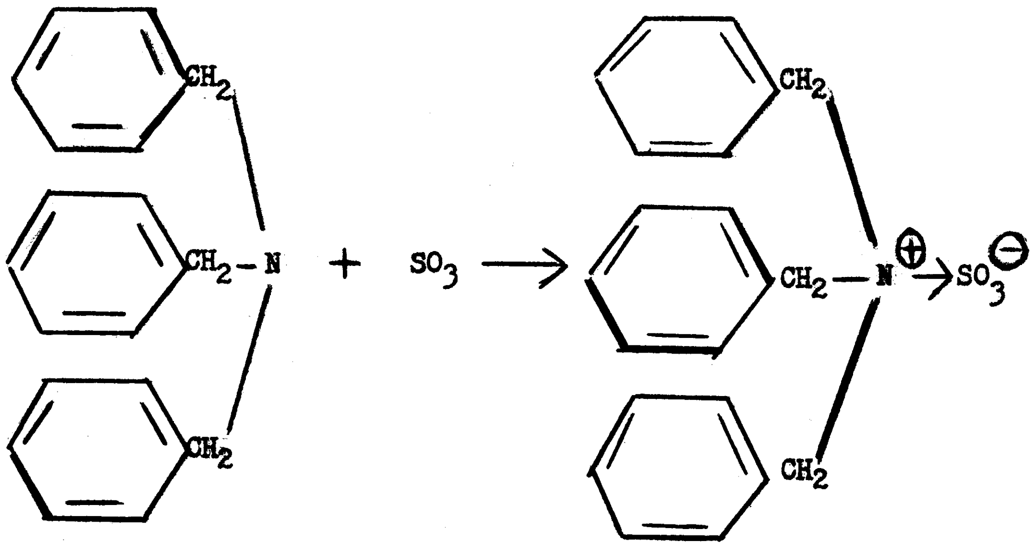
Triethylamine



Tributylamine

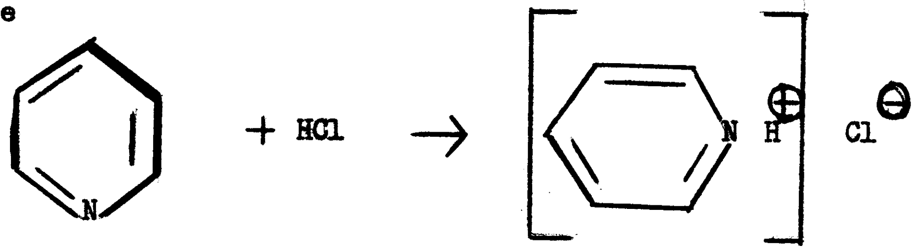


Tribenzylamine

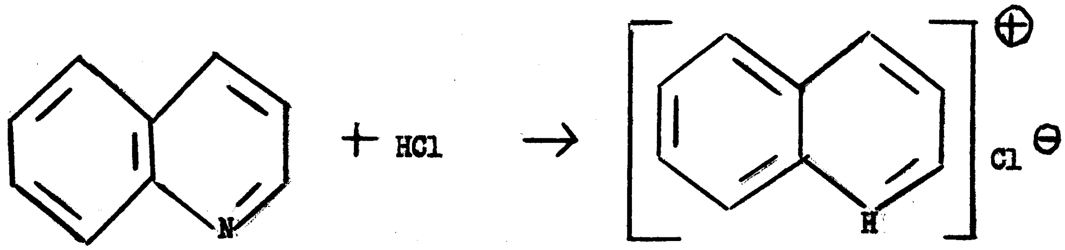


We have suggested a new method of generating hydrogen chloride gas by reacting 30 N sulfuric acid with sodium chloride and by scrubbing the gas with dual gas washers to remove water and impurities. We tried to produce tertiary amine hydrochloride salts by passing the scrubbed hydrogen chloride with dual washers into a 10% solution of the amine in ether. This method proved to be very successful since we were able to generate seven different tertiary amine hydrochlorides with complete success. The following reactions describe the tertiary amine hydrochloride derivatives that were prepared.

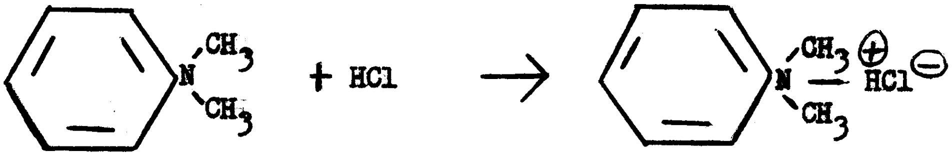
Pyridine



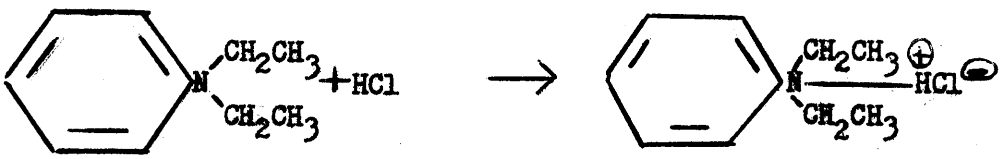
Quinoline



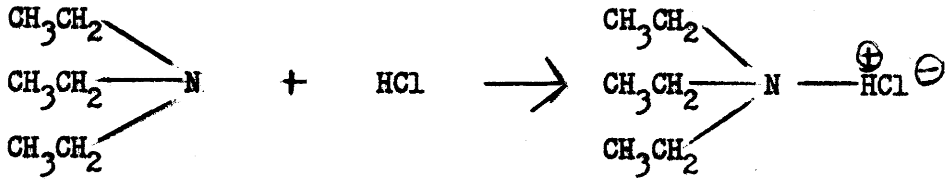
N-N Dimethylaniline



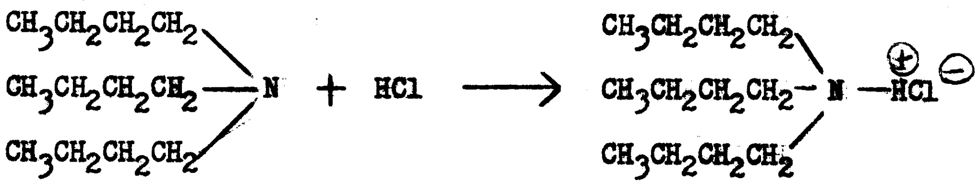
N-N Diethylaniline



Triethylamine



Tributylamine



Tribenzylamine

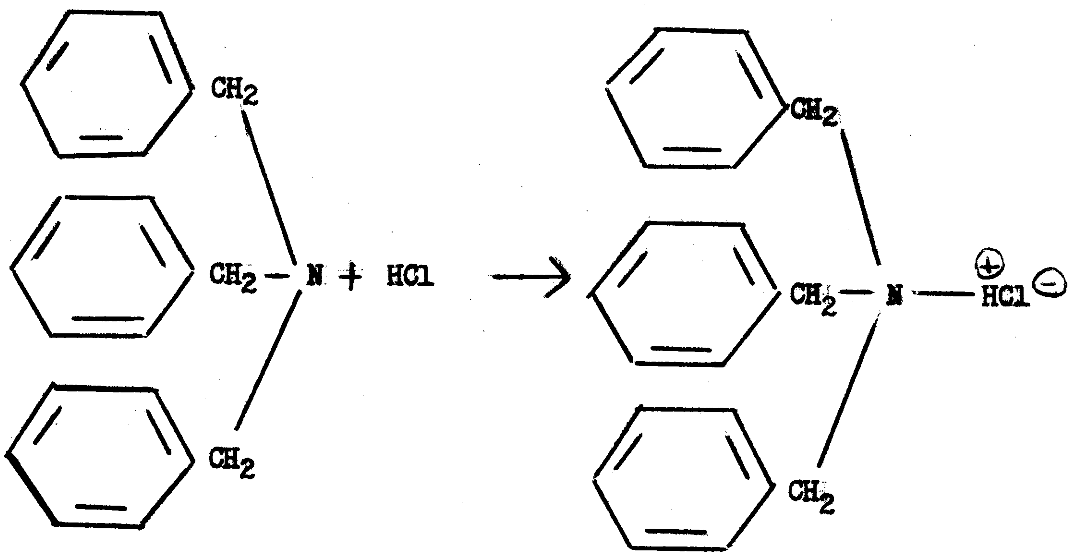


TABLE IV

TERTIARY AMINE SULFONATES

Compound	Observed Melting Point °C	
Pyridine Sulfonate	137 °C	(24)
2-Picoline Sulfonate	315 --- 320	(25)
Quinoline Sulfonate	270	(26)
N-N Dimethylaniline Sulfonate	85 and 90	(27)
N-N Diethylaniline Sulfonate	80 --- 100	(28)
Triethylamine Sulfonate	91.5	(29)
Tributylamine Sulfonate	94	(30)
Tribenzylamine Sulfonate	106 --- 107	(31)

The four easiest tertiary amine hydrochlorides to prepare were hydrochlorides of triethylamine, tributylamine, tribenzylamine, and N-N diethylaniline. Each formed a crystalline product readily in ether which was removed easily. The crystalline products were properly dried and produced sharp melting points. There was some variation in the melting points with the reported experimental values for the tertiary amine hydrochlorides.

The tertiary amine hydrochloride derivatives of pyridine, quinoline, and N-N dimethylaniline formed insoluble products very rapidly but were difficult to isolate because each is hygroscopic. The N-N dimethylaniline derivative was the hardest to prepare because it readily formed an oil, instead of a crystalline product. If the addition of hydrogen chloride gas was done slowly, this prevented the formation of an oil derivative. The N-N dimethylaniline and pyridine hydrochlorides had to be carefully removed under a dry methane or nitrogen atmosphere because the crystals are extremely hydroscopic. The quinoline hydrochloride derivative was formed readily but absorbed water rapidly from its surroundings. The quinoline hydrochloride derivative was oxidized by the air as evidenced by discoloration, resulting in an inaccurate melting point. The melting points of the seven tertiary amine hydrochloride derivatives are listed in Table V.

From the experimental evidence one can conclude that the technique of generating hydrogen chloride with the action of concentrated sulfuric acid upon hydrochloric acid or sodium

TABLE V

TERTIARY AMINE HYDROCHLORIDES PREPARED WITH PURE HYDROGEN CHLORIDE

Compound	Melting Point Crude Salt °C	Melting Point Pure Salt °C	Literature Melting Point °C	
Pyridine Hydrochloride	142-144°C	143-145(s)°C*	144.5°C 82	(32) (33)
Quinoline Hydrochloride	90-108	90-100(h) **	94 135	(34) (35)
N-N Dimethylaniline Hydrochloride	75- 85	85(s)	70- 75 85- 95	(36) (37)
N-N Diethylaniline Hydrochloride		155(s)	158	(38)
Triethylamine Hydrochloride	254-256	255-256(s)	253-254 254-255	(39) (40)
Tributylamine Hydrochloride		266-267(s)	256-257 310	(41) (42)
Tribenzylamine Hydrochloride	226-228	233-234(s)	227-228	(43)

* Sharp melting point

**Hydroscopic

chloride will contain sulfur trioxide contamination. This contamination can definitely account for some of the variations in the melting point of various amine hydrochlorides.

Since anhydrous salts were obtained it was possible that ethyl ether might be coprecipitating as an oxonium chloride. However, reaction was never carried to the point of complete amine precipitation and little of the less basic ether should then react. It was also noted that variations in melting point were equally prevalent with tertiary amine hydrochlorides produced in anhydrous benzene.

Our experimental data indicates that hydrate formation or molecular rearrangements are not satisfactory explanations of melting point variations. The possibility of errors in the melting point still can exist since many amine hydrochloride derivatives are hydroscopic. These hydroscopic amine hydrochlorides can form hydrates easily and produce slight deviations in their melting point.

The heating rates of the solid derivative in a capillary may lead to errors in the melting point but this can be controlled by careful techniques. A student in organic qualitative analysis should be aware of discrepancies in the melting points caused by heating rates. The student must expect slight deviations of 1° to 2°C in the observed melting point when compared to the reported value in the literature.

The amine hydrochloride derivative should be considered as a poor choice in the identification of amines. The melting point of many amine hydrochlorides have different reported values in the chemical literature. Many amine hydrochlorides were prepared from the year 1880 to 1950 before some improved techniques became available for their production. Some new techniques that have been developed recently are melting point determination using electronic devices; purity studies using ultraviolet, infrared, and other electronic apparatus; and modern devices for the prevention of hydrate formation. An important study that could be conducted is a complete revision of the melting points of many amine hydrochlorides. The discrepancies of literature values for a few amine hydrochlorides are given in Table VI.

If one intends to utilize the technique of generating hydrogen chloride by the action of concentrated sulfuric acid upon either dry sodium chloride or concentrated hydrochloric acid, he should consider the possibility of impurities. These impurities can be passed into the product which then produces variations in the melting point. In an organic qualitative analysis course, the melting point of a derivative is one technique employed in the identification of an organic compound. If variations in the melting point do exist in a particular derivative this possibly could result in the improper identification of an organic species. This is a particular difficulty that exists with the production of amine hydrochlorides because many discrepancies do appear in the literature melting point. A student in organic qualitative analysis course could have a difficult time trying to identify an amine by the use of a hydrochloride

TABLE VI

DISCREPANCIES IN LITERATURE MELTING POINT VALUES

Compound	Observed Melting Points °C			
Pyridine Hydrochloride	82°C	(44)	144.5°C	(50)
Quinoline Hydrochloride	94	(45)	135	(51)
Triethylamine Hydrochloride	253-254	(46)	254-255	(52)
N-N Dimethylaniline Hydrochloride	70- 75	(47)	85- 95	(53)
Piperidine Hydrochloride	237	(48)	244-245	(54)
Tributylamine Hydrochloride	256-257	(49)	310	(55)

derivative. Depending on the chemical techniques, a student may produce an amine hydrochloride that would possibly have a melting point that disagrees with the literature value. He may identify the wrong amine by comparing his experimental data with the literature values of amine hydrochlorides.

Many sources suggest not to use hydrochlorides as a derivative of tertiary amines. The explanation often cited is that the hydrochloride salts melt with decomposition that depends upon heating rates.[56] The decomposition of a hydrochloride salt could be explained on the basis that the derivative may contain impurities in the form of sulfonate.

CHAPTER IV

EXPERIMENTAL SECTION

All melting points were taken in capillaries in an electrically heated oil bath equiped with a constant stirring mechanism using a calibrated thermometer.

A. Detection of Sulfur Trioxide

Generation of hydrogen chloride was accomplished by adding 50 ml. of concentrated sulfuric acid to 50 g. of dry sodium chloride. The addition of sulfuric acid was done rapidly to produce an excess amount of hydrogen chloride that was passed into a saturated solution (1 g./ ml.) of barium chloride. A 50 ml. solution of freshly prepared and filtered saturated barium chloride was used for each trial. A white precipitate would be immediately formed as the hydrogen chloride passed into the saturated solution. The precipitate was identified as barium sulfate. The identical procedure was repeated except a single standard gas scrubber containing 250 ml. of concentrated sulfuric acid or an approximate depth of 15 cm. was used. A slight white precipitate was observed in a saturated barium chloride solution after generating hydrogen chloride into it for five to ten minutes. The precipitate was identified again as barium sulfate. This procedure was repeated ten times to study the various amounts of barium sulfate produced. Interest was also expressed in the reproduceability of this experiment to insure the identity of sulfur trioxide by the precipitation of barium sulfate.

Examining the effects of heating the mixture of sulfuric acid and sodium chloride to generate the hydrogen chloride gas, this usually resulted in a larger amount of white barium sulfate precipitate when compared to the rapid addition of sulfuric acid.

B. Elimination of Sulfur Trioxide

The generation of hydrogen chloride gas by reacting 50 ml. of concentrated sulfuric acid and 50 g. of dry sodium chloride was effective only if hydrogen chloride was passed very slowly through a single gas washer filled with at least 15 cm. of concentrated sulfuric acid at the approximate rate of one bubble per second. By adding the hydrogen chloride very slowly for thirty minutes, this appeared to remove most impurities from the vapors. The method is difficult because concentrated sulfuric acid reacts vigorously with sodium chloride and produces hydrogen chloride at various rates instead of at a steady rate. It was found that a dual gas washer filled with at least 15 cm. of concentrated sulfuric acid in tandom was the most effective method because the hydrogen chloride could pass through more scrubbing surface. Therefore, slow addition of sulfuric acid to sodium chloride and scrubbing the hydrogen chloride through a dual washer is considered the best technique to eliminate sulfur trioxide and water.

The use of 30 N sulfuric acid was more effective than the use of concentrated sulfuric acid. Reducing the concentration seemed to help prevent some local hot spots in the sodium chloride. The hydrogen chloride was passed through a dual washer to guarantee that the sulfur trioxide contamination would be eliminated.

The hydrogen chloride was passed through a 10 cm. drying tube containing anhydrous calcium chloride. But this method was found to be less effective in eliminating sulfur trioxide than using a single gas washer. Even slow addition of hydrogen chloride through the anhydrous calcium chloride did not reduce the amount of sulfur trioxide sufficiently.

C. Production of Amine Sulfonates

Sulfur trioxide was obtained by heating 50 ml. of fuming sulfuric acid. This provided a sufficient amount of sulfur trioxide to react with a 10% solution of the amine in ethyl ether. The 10% solution was prepared by adding 2.5 ml. of the particular amine and diluting to 25 ml. with ethyl ether. For tribenzylamine, a solid, we used a 2.5 g. sample and dissolved it in 25 ml. of ethyl ether. The sulfur trioxide was passed directly into the amine solution for thirty minutes to produce a solid salt.

Eastman Kodak Company reagent grades of Pyridine, 2-Picoline, Quinoline, Dimethylaniline, Diethylaniline, Triethylamine, Tributylamine, and Tribenzylamine were used. Analysis by titration to check purity was employed indicating 100% purity within experimental error.

The following sulfur trioxide derivatives were prepared by passing sulfur trioxide from heated fuming sulfuric acid into solutions of Pyridine, 2-Picoline, Quinoline, Dimethylaniline, Diethylaniline, Triethylamine, Tributylamine, and Tribenzylamine in ethyl ether. The melting points of the salt derivatives were Pyridine-Sulfonate, M. P. 137°C; 2-Picoline-Sulfonate, M.P. 314-319°C; Quinoline-Sulfonate, M. P. 269-270°C; N-N Dimethylaniline-Sulfonate, M. P. 84-85°C; N-N Diethylaniline-Sulfonate, M. P. 90°C; Triethylamine-Sulfonate, M. P. 91°C; Tributylamine-Sulfonate, M. P. 94°C; and Tribenzylamine-Sulfonate, M. P. 106-107°C.

It was necessary to recrystallize N-N Dimethylaniline-Sulfonate, Triethylamine-Sulfonate, and Tributylamine-Sulfonate from petroleum ether.

D. Production of Amine Hydrochlorides

A diagram of the apparatus used is given in Figure 2. Hydrogen chloride was obtained by adding 30 N sulfuric acid to dry sodium chloride and passing the gaseous substance into dual standard gas washers filled with at least 15 cm. of concentrated sulfuric acid. Then the dried and purified hydrogen chloride was passed for thirty minutes into a 10% solution of the amine in ethyl ether. The 10% solution was produced by adding 2.5 ml. of the amine and diluting to 25 ml. with ethyl ether. Again a 2.5 g. sample of tribenzylamine was dissolved in 25 ml. of ethyl ether. The hydrogen chloride reacts with the amine to produce a solid insoluble salt.

Eastman Kodak Company reagent grades of Pyridine, Quinoline, Dimethylaniline, Diethylaniline, Triethylamine, Tributylamine, and

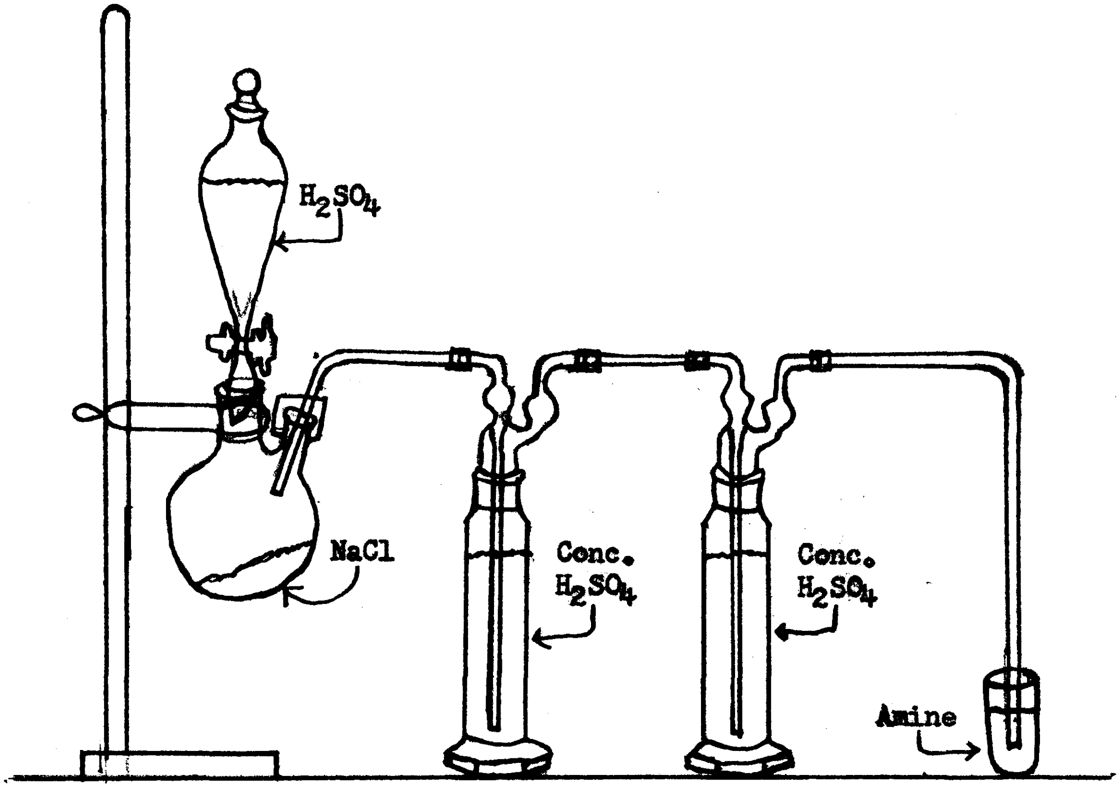


FIGURE 2

DIAGRAM OF APPARATUS USED IN THE PRODUCTION
OF PURE AMINE HYDROCHLORIDES

and Tribenzylamine were used. The purity was checked by analysis of titration, and purity of 100% was found within experimental error.

1. Pyridine Hydrochloride. This compound has a melting point of 143-145°C and was prepared by the manner described above. The crystalline product was very hygroscopic. The product was filtered under a dry atmosphere of methane and dried for forty-eight hours at 10 torr. The product was washed with petroleum ether and again dried for forty-eight hours to obtain its melting point.

2. Quinoline Hydrochloride. This compound was prepared in the identical manner described for pyridine hydrochloride. The product was dried for a period of forty-eight hours at 10 torr. The product was easily oxidized by air because the product was decolorized during its drying period. The product gave a poor melting point because it could not be isolated rapidly enough. The crude salt melted between 90-108°C and the salt washed with petroleum ether and dried for forty-eight hours at 10 torr. melted between 90-100°C.

3. N-N Dimethylaniline Hydrochloride. This hydrochloride was prepared in the manner that we designed to eliminate the production of impurities. This product often produces an oil derivative instead of a crystalline salt. It was found that very slow addition of hydrogen chloride would produce a crystalline product. The salt must be filtered off under dry methane atmosphere and dried for forty-eight hours at 10 torr. This product gave a sharp melting point at 85°C.

4. N-N Diethylaniline Hydrochloride. This compound was produced in the same manner as described for N-N dimethylaniline hydrochloride. It forms a crystalline product readily and can be isolated rapidly. The product was decolorized with activated charcoal and washed with petroleum ether. The derivative gave a sharp melting point at 155°C.

5. Triethylamine Hydrochloride. This hydrochloride was prepared in the manner described above. The crystalline product was formed rapidly and the crude salt melted at 253-254°C. The product washed with petroleum ether melted sharply at 255-256°C.

6. Tributylamine Hydrochloride. This compound was prepared in the identical manner as for triethylamine hydrochloride. The crystalline product was formed rapidly and was washed with petroleum ether. The dried product melted at 266-267°C.

7. Tribenzylamine Hydrochloride. This hydrochloride was prepared by adding 2.5 g. of the solid to 25 ml. of ethyl ether and passing the dried hydrogen chloride into the solution for thirty minutes. This product was the easiest to isolate and handle. The crude salt melted at 226-228°C and the salt washed with petroleum ether melted at 233-234°C.

CHAPTER V

SUMMARY

In this study we have attempted to explain the inconsistences in the melting point of amine hydrochlorides. The variations of 10-20°C in the melting points can be explained on the basis of impurities that are contained in the solid salt. We have demonstrated by this study that sulfur trioxide will be produced as a by-product generated by the action of concentrated sulfuric acid upon either dry sodium chloride or concentrated hydrochloric acid. The sulfur trioxide will readily react with an amine to produce an amine sulfonate. The amine hydrochloride product from hydrogen chloride so generated will contain some sulfonate impurities that produce variations in the melting point. Some discrepancies in the melting point of amine hydrochlorides exist because many amines are hydroscopic.

The problems complicating the preparation a pure amine hydrochloride are: (1) the addition rates of concentrated sulfuric acid to dry sodium chloride or concentrated hydrochloric acid, (2) the addition rates of hydrogen chloride to an amine, (3) concentration of sulfuric acid, (4) proper scrubbing of the hydrogen chloride, and (5) the sulfonate impurities.

The following suggestions may be used to solve the problems complicating the preparation of a pure amine hydrochloride:

(1) The slow addition of concentrated sulfuric acid to either dry sodium chloride or concentrated hydrochloric acid will prevent the possible decomposition of sulfuric acid into sulfur trioxide and water.

(2) The slow addition of the hydrogen chloride to an amine solution will help to prevent the possible occurrence of an oil derivative.

(3) The 30 N sulfuric acid will help to reduce the likelihood of hot spots in the sodium chloride or hydrochloric acid and therefore reduce the amount of sulfur trioxide generated.

(4) It is important to wash the hydrogen chloride in dual gas washers filled to a depth of 15 cm. with concentrated sulfuric acid to remove water and sulfur trioxide. We have shown that slow addition of sulfuric acid and dual washers are effective and should remove the sulfur trioxide.

(5) If all of the previous steps are employed, the elimination of sulfur trioxide will be accomplished. The elimination of sulfur trioxide should prevent the possible occurrence of an amine sulfonate. Therefore some of the problems complicating the preparation of a pure amine hydrochloride should be solved.

If possible, another method of generating hydrogen chloride should be found to eliminate the possibility of impurities contained in the solid salt. An extensive search in the literature should be made to find an alternate method of producing amine hydrochlorides. Whenever possible another derivative of a tertiary amine should be used because the amine hydrochlorides have many reported discrepancies in their melting points.

Students in organic qualitative analysis may be encouraged to use hydrochlorides as derivatives of tertiary amines only with the following qualifications:

(1) All amine hydrochlorides should be produced with the purest

hydrogen chloride available.

(2) Literature values for the melting points of tertiary amine hydrochlorides are subject to question. Observed melting points should be compared with control samples.

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