THE CHLORINATION OF AQUEOUS SUSPENSIONS
OF ABIETIC ACID

By

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION

It is only natural that a compound as cheap and as plentiful as abietic acid should be subjected to extensive laboratory investigation. It has been reported to undergo numerous reactions including halogenation, and several methods have been proposed in the literature for the preparation of chloride addition products of abietic acid. However, the treatment prescribed in most cases proved much too severe and only served to increase the rate at which the already unstable chlorination product dehydrohalogenated after formation. As a result, no chlorine containing compound could be separated when others attempted to reproduce these methods. The purpose of this work was to establish that done in 1951 on a reproducible basis and to determine whether a stable chloride addition product could be prepared.

HISTORICAL BACKGROUND

Abietic acid occurs as one of the chief products in the nonvolatile fraction of the oleoresin from the American pine tree, Pinus abies. It, together with two of its isomers, (neoabietic and levopimaric,) comprises 40% of this nonvolatile fraction. In the form of rosin, one of its main uses for many years has been caulking for the hulls of wooden ships and the weatherproofing of ropes.

Abietic acid was first isolated by Baup in 1826 and since then has been the subject of much investigation. It is a light yellow to white crystalline solid, melting at 133°-166° C. and having the molecular formula $C_{20}H_{30}O_2$. Dehydrogenation, using a palladium-charcoal catalyst at temperatures of 300°-330° C., yields 90% retene, 4 moles of hydrogen, 1 mole of methane, 0.75 moles of carbon dioxide, and 0.25 moles of carbon monoxide.(1) This is taken as proof that abietic acid has as its nucleus a partially hydrogenated phenanthrene ring. Investigation has shown also that abietic acid has two points of unsaturation occurring at the 7,8 and 9,14 positions on the ring.(2)

Crude abietic acid is readily isolated from rosin by the action of acids or heat, either of which serves to convert its two bond labile isomers, neoabietic and levopimaric, to abietic acid.

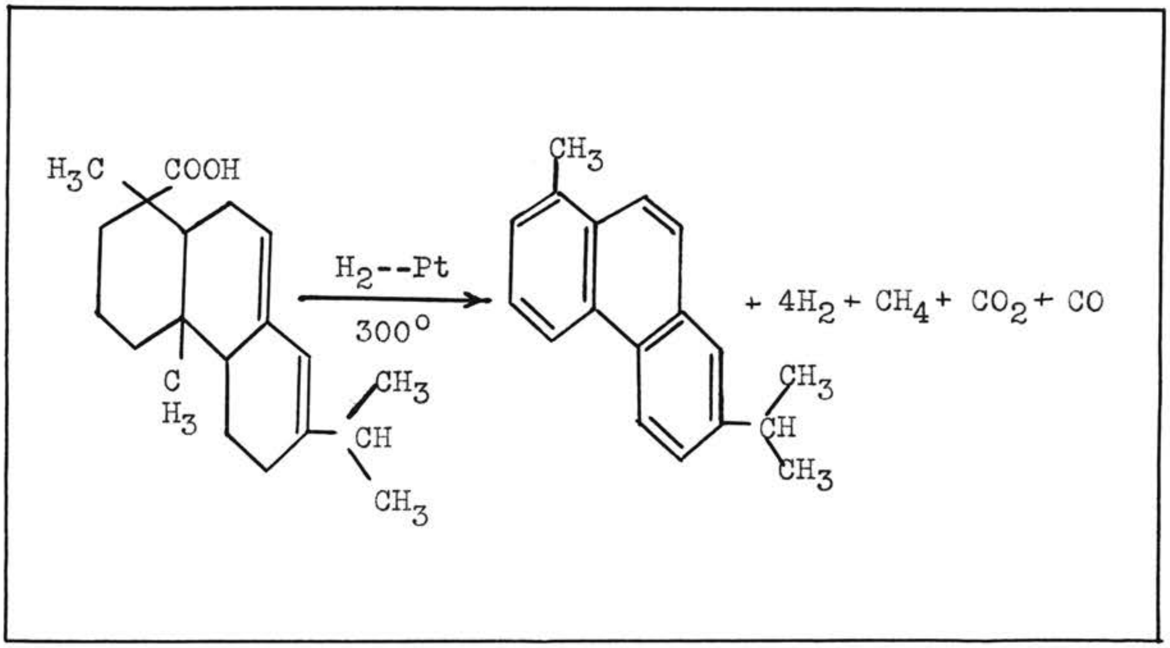

FIGURE 1. THE DEHYDROGENATION OF ABIETIC ACID

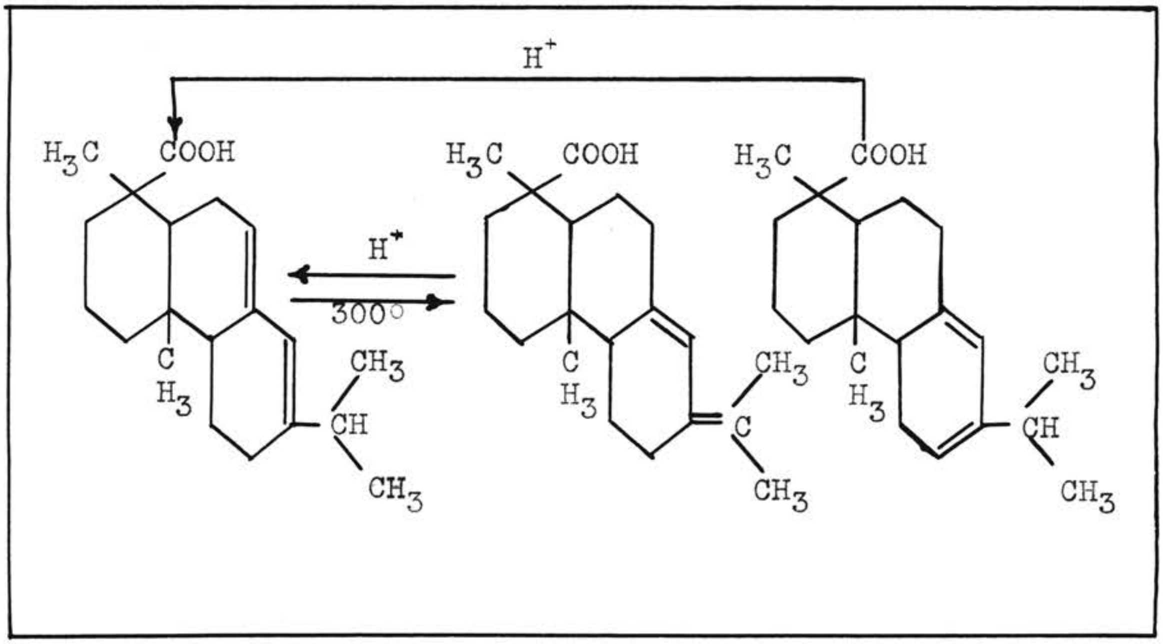

FIGURE 2. THE ISOMERIZATION OF ABIETIC ACID (3)

Abietic acid is one of the cheapest and most abundant of the higher molecular weight organic acids and has been used in the manufacture of low grade soaps, paper sizes, varnishes, plastics, and many other products. Being such a plentiful and cheap raw material, it is only natural that abietic acid should be subjected to extensive laboratory investigation. Attempts have been made to oxidize, esterify, ammonolyze, brominate, and chlorinate abietic acid, and these attempts have met with varying degrees of success. Only if the acid is first completely hydrogenated is it possible to prepare its esters and acid chloride. The carboxyl group, after such treatment, appears much more stable toward heat. Such a hydrogenation must be carried out under elevated temperatures and pressures, since under ordinary conditions it is almost impossible to saturate the molecule. Under laboratory conditions, using Adams' catalyst, the molecule is seen to add one mole of hydrogen almost immediately, but then the rate of absorption tapers off and comes almost to a halt without fully saturating the second double bond.

As yet no one has succeeded in preparing a stable chloride addition product of abietic acid. Among the methods that have been suggested in the literature for the chlorination of abietic acid are: agitation of the acid in a solution of calcium hypochlorite at 0°-30° C.(4); direct chlorination in actinic light, using temperatures up to 200° C. (5); treatment with sodium hypochlorite in chloroform (6); chlorination in an inert solvent such as chloroform or carbontetrachloride, using a metallic halide such as aluminum chloride as a catalyst and temperatures of 50°-125° C. (7); and chlorination of aqueous suspensions at room temperature (8). None of the above methods, with the exception of the last mentioned, yielded a chlorine containing compound when attempts were made to duplicate these methods. The one described by Borglin (7) resulted in a high molecular weight polymer which contained no chlorine, could not be ignited, and was insoluble in all common laboratory solvents (9).

Bobst (10) managed to obtain some chlorination products containing up to 27% chlorine, but these compounds proved to be unstable, undergoing dehydrohalogenation on standing. The compounds which he prepared in non-aqueous solvents proved to be less stable than those prepared from aqueous suspensions. Those prepared at 0° C. in non-aqueous solvents were least stable of all, evolving hydrogen chloride immediately after preparation. The most stable of Bobst's compounds, those prepared from aqueous suspensions at room temperature, held together for only two to three months before beginning to evolve noticeable amounts of hydrogen chloride.

EXPERIMENTAL WORK

The Purification of Abietic Acid

An attempt was made to recrystallize a kilogram of technical grade abietic acid from hot methanol. When the acid failed to crystallize out, it was thought that it had probably undergone autoxidation and isomerization on standing. On this assumption an attempt was made to liberate the acid by Steele's method (11). Approximately three hundred fifty grams of the technical grade acid were placed in a one-liter round-bottom flask together with two hundred fifty grams of glacial acetic acid and heated under reflux for a period of four hours. The flask was then cooled to room temperature. When no crystals appeared more acid was added, and the solution was heated for another four hours. Progressively larger amounts of abietic acid were added to the mixture, which was refluxed for longer and longer periods of time with no crystals resulting upon cooling. After over a kilogram of abietic acid had been added to the flask without resulting in the formation of a crystalline product, a mass of glass wool was placed in it. The flask was then stoppered and set aside for a period of three months. At the end of that time the amount of the crystalline acid that was recovered was only fifteen grams.

Since the purification of the technical grade acid proved unsuccessful, probably because of the extreme autoxidation of the acid while in storage, an attempt was made to isolate the acid from commercial grade rosin, using the method described by Steele. About three pounds of rosin were placed in a two-liter round-bottom flask together with five hundred milliliters of glacial acetic acid and heated under reflux for twenty-four hours. At the end of this time the hot solution was poured into a large beaker and allowed to cool slowly to room temperature. The resulting crystals were then filtered by suction through a large Buchner funnel, dried, and recrystallized four times from just enough hot methanol to get the acid completely into solution. This treatment yielded a light yellow crystalline solid having a melting point of 149°-156° C. and a neutralization equivalent of 304.

Analytical Procedures

The following analytical procedures were used to determine the chemical constitution and physical properties of abietic acid and its chlorination products:

Chlorine analysis. The total percentage of chlorine in the reaction products was determined by ignition, using a Parr Peroxide Bomb. An accurately weighed sample of the chlorination product ranging between one hundred and two hundred milligrams was placed in the ignition crucible of the bomb together with five tenths of a gram of benzoic acid and one scoop of high purity sodium peroxide. A length of Parr fuse wire seven centimeters long was connected to the leads in the bomb head, and the bomb was then assembled. After the head of the bomb had been tightened down with a wrench, the bomb was shaken for several minutes to mix the contents thoroughly. It was then tapped sharply on the desk several times to pack down the contents and placed in the Parr water bath assembly, where it was fired electrically. The bomb was allowed to cool to room temperature, after which it was removed from the water bath, dried, and opened. The bomb head was carefully rinsed with distilled water, and the rinsings were collected in a four hundred milliliter beaker. The ignition crucible was placed in the beaker, to which was added two hundred fifty milliliters of distilled water. The beaker was covered with a watch glass and warmed to dissolve the fused material and to destroy any excess peroxide. The crucible was then removed from the beaker and rinsed carefully; the rinsings were collected in the beaker. After the solution was allowed to cool, it was filtered to remove any free carbon and particles of fuse wire. It was then acidified with nitric acid, and the solution was boiled for several minutes to expel any carbon dioxide present. From this point, the analysis proceeded in one of three ways:

A. Gravimetric chloride analysis.

When the chloride was to be determined gravimetrically, the solutions were allowed to cool after boiling. Fifty milliliters of approximately one tenth normal silver nitrate were added to each beaker, and the beakers were placed in a dark place to allow the precipitate to settle. The solutions were then filtered by suction through accurately weighed, medium frit, pyrex crucibles. The precipitates were rinsed several times with distilled water, and the crucibles were placed in a drying oven at 100°-110° C. for thirty to sixty minutes. At the end of this time the crucibles were removed from the oven, cooled in a desiccator, and weighed. The percentage of chlorine was calculated using the following formula:

$$\%\ \text{Cl} = \frac{\text{Wt. of AgCl} \times 0.24737}{\text{Wt. of sample}} \times 100$$

B. Mohr volumetric chloride analysis.

In the volumetric chloride determination by the Mohr method, the pH of the solution was carefully adjusted to between six and seven by the addition of sodium bicarbonate. About one milliliter of five percent potassium carbonate was added to the solution, which was then titrated with a standard solution of one tenth normal silver nitrate until a definite orange color appeared. The percentage of chlorine was calculated by the following formula:

$$\%\ \text{Cl} = \frac{\text{Ml of AgNO}_3 \times \text{N of AgNO}_3 \times 0.35457}{\text{Wt. of sample}} \times 100$$

C. Potentiometric volumetric chloride analysis.

In this method, the Fisher Titrimeter was used. The solution to be analyzed was transferred to an electrolytic beaker equipped with a magnetic stirrer. This beaker was joined to a second beaker containing a one tenth normal solution of potassium chloride by an agar-ammonium nitrate salt bridge, which was prepared by filling a "U" tube with a hot solution of one tenth normal ammonium nitrate containing three percent agar and cooling it. In the beaker containing the chlorine unknown was placed a silver/silver chloride electrode, and in the beaker containing the potassium chloride solution was placed a saturated calomel electrode. The electrodes were then connected to the terminals of the titrimeter, and the titrimeter was calibrated as described by Willard, Merrit, and Dean (12). The chloride sample was titrated with a standard solution of one tenth normal silver nitrate. The end point was taken as that volume at which a maximum change in voltage was observed for a minimum change in volume. The percentage of chlorine was calculated in the same manner as described for the Mohr method above.

Neutralization equivalent. The neutralization equivalent of abietic acid and its chlorination products was determined in the following manner: an accurately weighed sample of material was placed in a two hundred fifty milliliter Erlenmeyer flask and dissolved in chemically pure methanol. Three to four drops of phenolphthalein were added to the solution, and the sample was titrated with a standard solution of one tenth normal potassium hydroxide in methanol.

In several cases, difficulties arose because the chlorination products of abietic acid themselves behaved as indicators, changing from colorless in acid solutions to deep yellow in basic solutions. The color change was observed to be a gradual one which almost completely covered up the color of the phenolphthalein. It was found that this situation could be remedied by the addition of distilled water in sufficient amounts to initiate the precipitation of the sample. After the addition of the water it was possible to carry out the titration in the usual manner.

A more satisfactory method for the determination of neutralization equivalents was found to be a potentiometric titration, using the Fisher Titrimeter. An accurately weighed sample was placed in an electrolytic beaker and dissolved in chemically pure methanol. A glass electrode and a saturated calomel electrode were placed in the beaker and connected to the terminals of the titrimeter. The titrimeter was calibrated and the titration was carried out in the usual manner. The end point was taken to be that point at which a maximum change in voltage occurred for a minimum addition of base.

In all cases, the neutralization equivalent was calculated by the following formula:

$$\text{N. E.} = \frac{\text{Wt. of sample} \times 1000}{\text{Ml of base} \times \text{N of base}}$$

Qualitative determination of hydroxyl groups. The presence of hydroxyl groups in the chlorination product was determined by the ferric hydroxamate test as described by Cheronis and Entrikin (13). Some of the chlorination product was placed in a large test tube with an equal volume of acetyl chloride and dimethylaniline and allowed to react for five minutes, during which time it was shaken at frequent intervals. Then several milliliters of cold water were added to decompose the excess acetyl chloride, and the mixture was poured into a six inch test tube. Two or three drops of the top layer in the test tube were transferred to another test tube, and to this was added five tenths of a milliliter of a one normal solution of hydroxylamine hydrochloride in methanol. To this solution was added enough potassium hydroxide in methanol to make the solution definitely alkaline to litmus. The solution was then heated to boiling and allowed to cool. It was acidified with dilute hydrochloric acid, and to the acidic solution a few drops of ten percent ferric chloride solution were added. The appearance of a reddish wine color was taken as a positive test.

Molecular weight. Attempts were made to determine the molecular weight of abietic acid and its chlorination products by the Beckman freezing point method, but these attempts proved unsuccessful. The purified abietic acid dimerized in all solvents in which it was soluble. In addition, the chlorination products evolved hydrogen chloride at such a rate as to cause a continuous increase in molecular weight values obtained from one determination to the next.

The Chlorination of Abietic Acid

Preliminary work. A sample of one of the more stable chlorination products prepared by Bobst (14) was obtained, and an attempt was made to determine its chemical and physical properties. It was hoped that, after analysis, the sample could be used as a standard in an attempt to reproduce his work.

At the time of its preparation, in 1951, Bobst reported the sample as containing 23% chlorine by weight. When the sample was analyzed for chlorine in 1953, using the Parr Peroxide Bomb and gravimetric chloride procedure, values were obtained ranging from 10.49% to 13.60%, the average being 12.47%.

An attempt was made to determine the molecular weight by the Beckman freezing point method. Since the product seemed to dimerize in most of the solvents it was soluble in, this method proved unsuccessful. The values obtained were erratic, ranging from 575 to 864.43. Most of the values seemed to be concentrated between 601 and 696. This was approximately twice the value predicted for the compound. The determination of molecular weights by the Rast method was not attempted because the compound decomposed when heated.

Since the usual methods for the determination of molecular weights failed to yield reasonable results, an attempt was made to determine the neutralization equivalent of the compound. Colorimetric determination of the neutralization equivalent of the compound yielded values of 310.7 to 374, with an average value of 331. These values were verified by the use of the Fisher Titrimeter, where an average value of 337 was obtained.

From the above information, it was calculated that only one chlorine atom was present per molecule of the compound.

The above information brought up the question of whether Bobst's sample was still undergoing dehydrohalogenation. To test this, about one gram of the sample was placed in a five hundred milliliter round-bottom flask with two hundred fifty milliliters of distilled water and boiled for several minutes. After the solution was cooled and filtered, the filtrate was tested for the presence of chloride ion by the addition of silver nitrate. A white precipitate of silver chloride indicated a positive test.

<u>Run 1</u>: This run was made to become familiar with the apparatus and the behavior of the products during reaction. The apparatus used was that described by Bobst (15) and illustrated in Figure 3. Fifty grams of abietic acid were

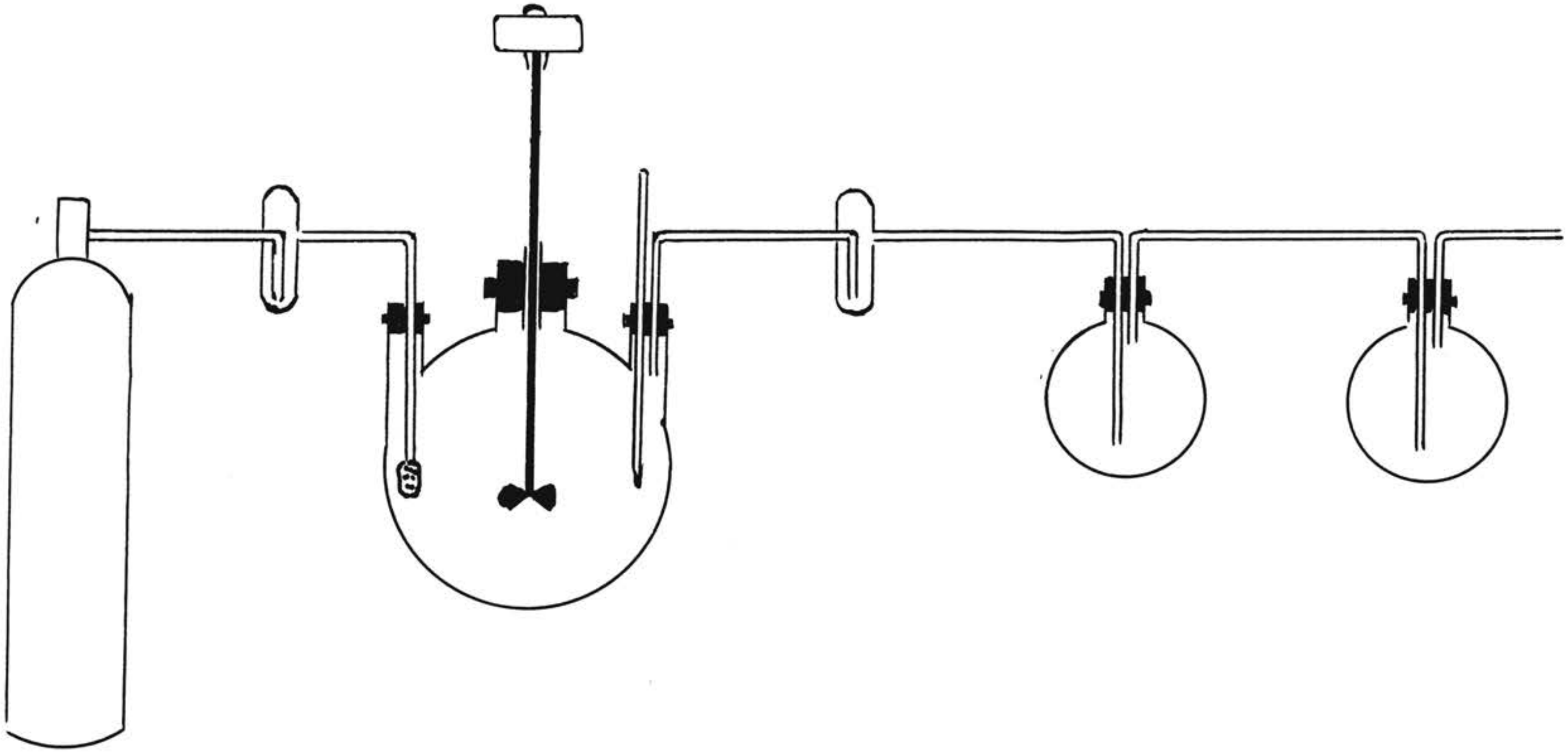

FIGURE 3. CHLORINATION APPARATUS AS DESCRIBED BY BOBST

placed in the reaction flask together with five tenths of a gram of iodine, two grams of potassium iodide, and three hundred milliliters of distilled water. At a fairly rapid rate for a period of four hours, chlorine was passed through the suspension of the acid with constant stirring. The temperature was kept below 30° C. At the end of four hours the reaction was suspended for two days. After resumption, the reaction had to be terminated almost immediately, however, because the contents of the outlet bubble counter and chlorine absorption train backed up into the reaction flask. The chlorination product in the reaction flask was filtered by suction, washed several times with distilled water, and dried. The product was a fine, white to light yellow powder. It had a faint chlorine odor, and it seemed to decompose when pressed between the fingers. The gravimetric analysis for chlorine gave values of 17.26% to 21.56%; the determination of the neutralization equivalent gave values of 520.57 to 538.57; the ferric hydroxamate test for hydroxyl groups was positive.

Run 2: Because of the difficulties encountered in run one, the apparatus was modified by inserting stopcocks between the reaction flask and the inlet and the outlet bubble counters as shown in Figure 4. Fifty grams of abietic acid were placed in the reaction flask, along with five tenths of a gram of iodine, two grams of potassium iodide, and four hundred milliliters of distilled water. Chlorine was passed through the suspension at a rapid rate, with

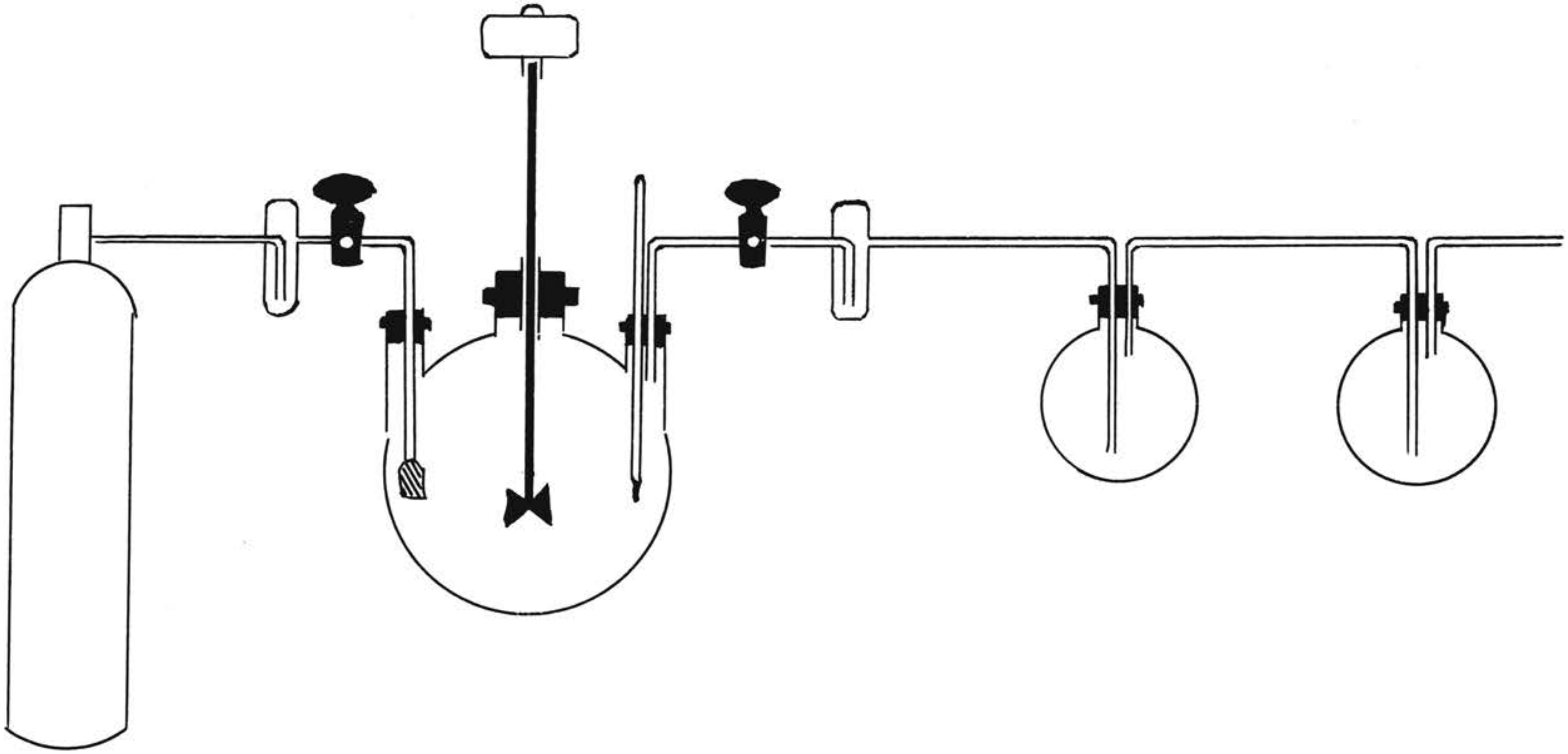

FIGURE 4. INITIAL MODIFICATION OF CHLORINATION APPARATUS

constant stirring for a period of fifteen hours, the temperature held fairly constant at 28° C. At the end of this time the material was filtered by suction, washed repeatedly with distilled water, and dried in air for a period of twenty-four hours. The product was light pink in color and again had a faint chlorine odor. The gravimetric chloride analysis gave values of 20.43% to 21.05% chlorine; the determination of neutralization equivalents gave values of 556.76 to 581.31; the test for hydroxyl groups was positive.

On the basis of the possibility that the pink coloration of the reaction product from run two might be caused by unsaturation in the molecule, the products from both runs one and two were tested to determine their relative stabilities toward heat. It was believed that the unsaturated compound should be more heat stable than the saturated one. Accurately weighed samples of the reaction products were placed in a drying oven at 85° C. for a period of twenty-six hours. At the end of this time, the samples were removed from the oven, their appearances noted, and the samples placed in a desiccator to cool. The reaction product from run one had turned dark brown in color and had fused slightly, while the reaction product from run two had turned a yellow-orange in color but had remained in a fine, powdery form. After cooling, the samples were reweighed and the percentage loss in weight calculated. The reaction product from run one was found to have lost 41.75% of its weight, while the reaction product from run two was found to have lost 36.68% of its weight. Gravimetric analysis for chlorine gave a value of 37.87% for the product of run one and 33.35% for the product of run two. A neutralization equivalent of zero was obtained for both samples, indicating that they had undergone decarboxylation during heating.

The stopcocks used in the apparatus in run two proved unsatisfactory because both ordinary stopcock grease and silicone stopcock grease were attacked by the free chlorine, forming very gummy substances which prevented the stopcocks from being opened or closed easily. For this reason, the stopcocks were removed, and traps were placed above the flasks in the absorption train as shown in Figure 5 to prevent their contents from reaching the reaction flask in the event of too rapid an absorption of chlorine.

<u>Run 3</u>: It was believed that the rate of absorption of chlorine could be increased if the temperature of the reaction mixture was held around 0° C. during the reaction. The reaction flask was equipped with a stainless steel stirrer and placed in an ice salt bath. Fifty grams of abietic acid were placed in the reaction flask together with five tenths of a gram of iodine and one gram of potassium iodide. A two hundred fifty milliliter portion of distilled water was added, and the suspension was stirred until the temperature in the flask reached 0° to 2° C. Chlorine was then passed rapidly into the reaction flask for four hours. It was noted that after two hours the

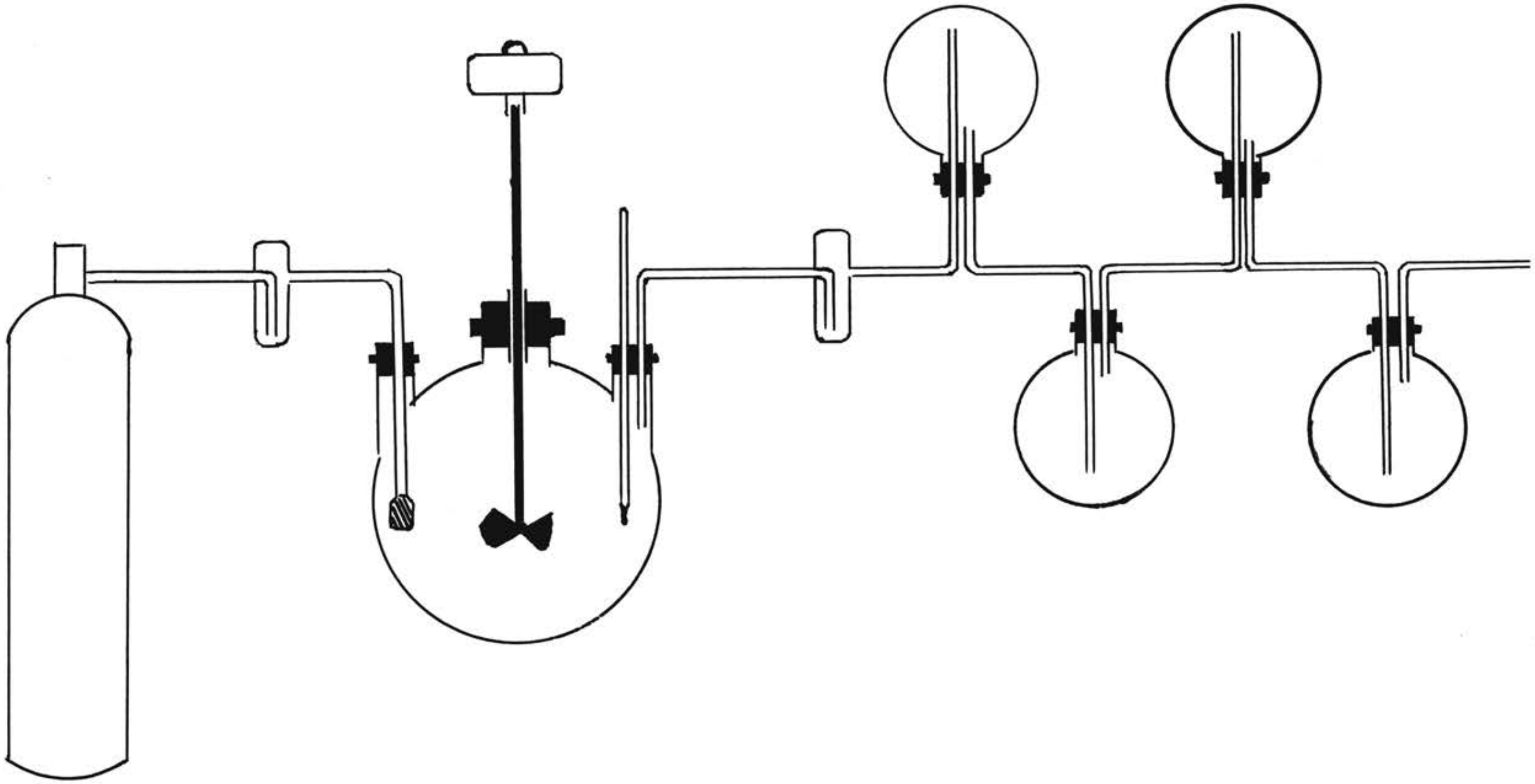

FIGURE 5. FURTHER MODIFICATION OF CHLORINATION APPARATUS

solution turned bright green. This color was later found to be caused by the fact that the metal stirrer had been attacked by the chlorine. At the end of four hours, the reaction was terminated; the product was filtered by suction, washed several times with distilled water, and dried in the air overnight. The product was then light green in color, but the color disappeared after frequent washings. The Mohr method of analysis for chlorine gave values of 20.01% to 20.45%. The ferric hydroxamate test for hydroxyl groups was positive.

Run 4: Run four was essentially the same as run three, with the exception that a pyrex stirrer was used in place of a stainless steel one. Fifty grams of abietic acid were placed in the reaction flask together with five tenths of a gram of iodine, one gram of potassium iodide, and four hundred milliliters of distilled water. The flask was cooled to between 0° and 3° C., and the mixture was chlorinated for four hours. At the end of this time the product was filtered, washed several times with distilled water, and air-dried overnight. The Mohr method of analysis for chlorine gave values of 23.98% to 23.99%; the determination of the neutralization equivalent gave a value of 435. The test for hydroxyl groups was positive.

The reaction product from run four was observed to evolve noticeable amounts of hydrogen chloride after standing only two weeks, although the reaction product from run three had not begun to evolve hydrogen chloride even after standing for more than two and one-half months. Both products had been prepared under the same conditions with the exception of the change in the type of stirrer used. An attempt was made to determine their relative stabilities toward heat in the same manner as the products in runs one and two. Accurately weighed samples were placed in an oven at 80° C. for seventy-two hours. The products were then removed from the oven, cooled, and weighed. The product of run three was found to have lost 32.36% of its weight, but the product from run four lost only 7.32% of its weight. Both samples were too badly decomposed to permit the determination of the percentage of chlorine or the neutralization equivalent.

<u>Run 5</u>: This run was essentially the same as run four except for the fact that the reaction was allowed to proceed for a longer period of time. Fifty grams of abietic acid were placed in the reaction flask together with five tenths of a gram of iodine, one gram of potassium iodide, and four hundred milliliters of distilled water. The reaction mixture was cooled to between 0° and 2° C., and chlorine was passed through the suspension at a fairly rapid rate with constant stirring for fourteen hours. At the end of this time the reaction was terminated. The product was filtered by suction, washed several times with distilled water, and allowed to dry overnight. Analysis for chlorine by the Mohr method gave values of 26.79% to 26.89%; determination of the neutralization equivalent gave values of 532 to 548. The test for hydroxyl groups was negative.

Run 6: This run was made for the purpose of determining what may have caused the more stable product in run three. Since nickel is one of the constituents of stainless steel, and since its chloride could account for the green coloration present in run three, it was decided to add a small amount of this substance to the reaction mixture. Fifty grams of abietic acid were added to the reaction flask together with five tenths of a gram of iodine, one gram of potassium iodide, fifty milliliters of a saturated solution of nickel chloride, and four hundred milliliters of distilled water. The reaction mixture was cooled to 0° C., and chlorine was passed rapidly through the suspension with constant stirring. When the reaction was started, it was hoped to continue chlorination for a period of seventy-two hours. It had to be terminated, however, after a period of only twenty-four hours because of excessive foaming. The extent of the foaming could not be reduced by the use of anti-foaming agents such as Dow-Corning Anti-Foam A and was later found to be caused by the sudden release of trapped chlorine when the temperature of the reaction mixture was allowed to rise above 5° C. The determination of chlorine by the Mohr method gave a value of 33.30% chlorine, and the test for hydroxyl groups was negative. The compound remained stable for only two or three weeks before beginning to evolve noticeable amounts of hydrogen chloride.

The difficulties encountered in run six led to further modification of the apparatus as shown in Figure 6. This

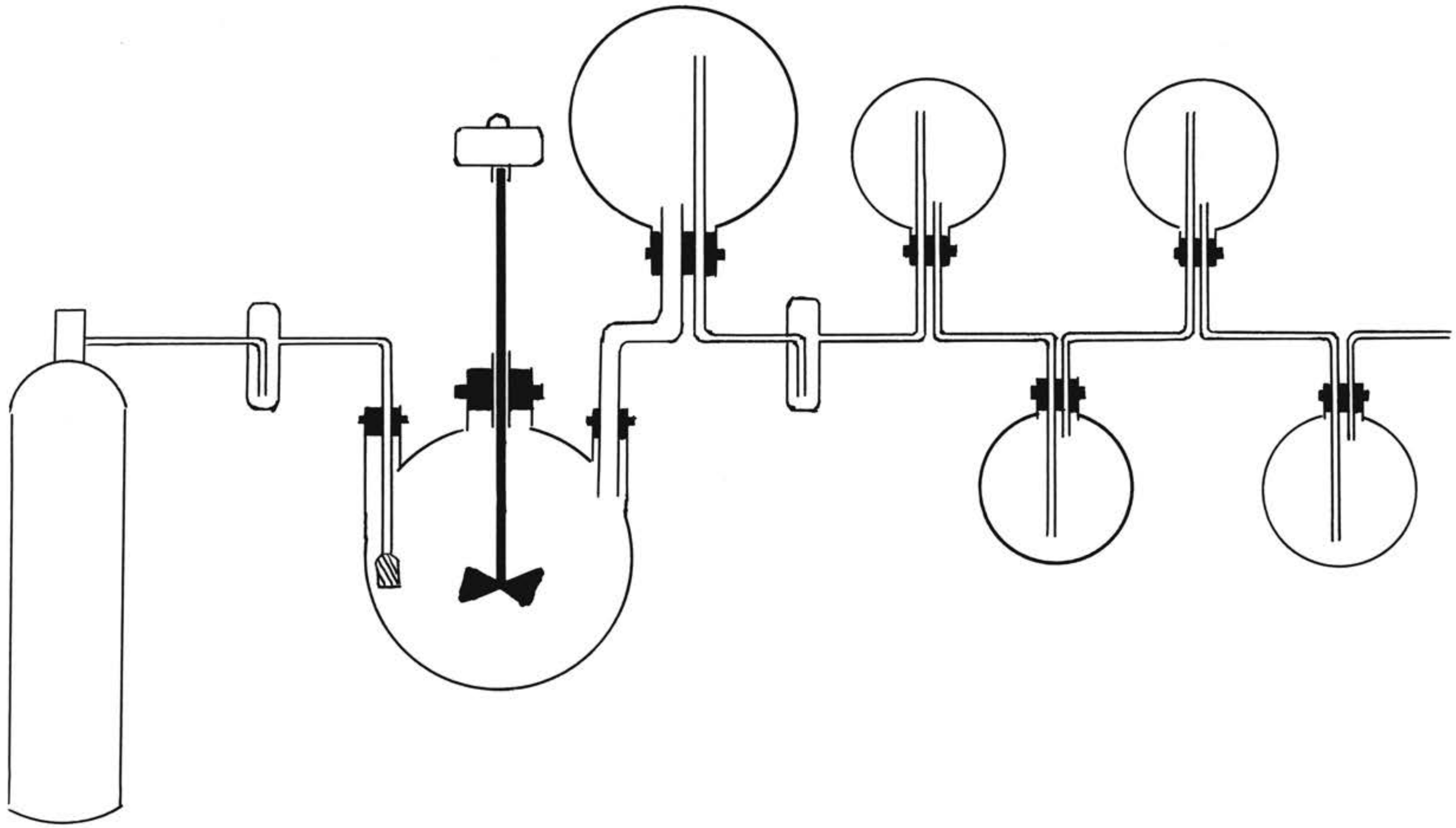

FIGURE 6. FINAL MODIFICATION OF CHLORINATION APPARATUS

final modification involved inserting a trap with a large outlet tube between the reaction flask and the outlet bubble counter.

Run 7: This run was made to determine whether the reaction was dependent on the use of a catalyst. Fifty grams of abietic acid were placed in the reaction flask with five hundred milliliters of distilled water. All other materials were omitted. Chlorine was passed through the suspension with constant stirring for fifty-six hours. At the end of this time the reaction was stopped; the product was filtered, washed repeatedly with distilled water, and dried in air overnight. The Mohr method of analysis gave values of 27.15% to 27.26% chlorine. The test for hydroxyl groups was negative. The compound was not found to be evolving noticeable amounts of hydrogen chloride even after standing two and one-half months. From this run it was concluded that the reaction was dependent on the use of a catalyst.

Run 8: Since the reaction product from run five proved unstable, run eight was made with chromium chloride utilized in the place of nickel chloride. Fifty grams of abietic acid were placed in the reaction flask with five tenths of a gram of iodine, one gram of potassium iodide, and fifty milliliters of a saturated solution of chromium chloride. After four hundred milliliters of distilled water had been added to the mixture, chlorine was passed through the solution for a period of twenty-four hours. The reaction was then terminated; the product was filtered by suction, washed repeatedly with distilled water, and dried overnight. The resulting product was a fine pink powder. The color was thought to be caused by the presence of free iodine, but repeated rinsings with distilled water and five percent potassium iodide solution failed to remove the tint. Analysis for chlorine by the Mohr method gave values of 26.82% to 26.94%; the test for hydroxyl groups was negative.

To study systematically the rate at which the chlorine added into the abietic acid molecule, the next four runs used the various catalysts that had been employed in previous runs. However, at intervals of one, two, three, four, eight, and sixteen hours during the reaction, samples were removed through the outlet neck of the reaction flask by the use of a one hundred milliliter pipet equipped with an atomizer bulb. The samples were filtered by suction, washed several times with distilled water, and dried. The products were analyzed for chlorine content, and the values obtained were plotted on a graph as shown in Figure 7, with the percentage of chlorine as the ordinate and the time in hours as the abscissa.

Run 9: Fifty grams of abietic acid were placed in the reaction flask with five tenths of a gram of iodine, one gram of potassium iodide, and fifty milliliters of a saturated solution of chromium chloride. Five hundred milliliters of distilled water were added to the mixture, and the solution was cooled to 4° C. Chlorine was then passed through the solution for sixteen hours. Chlorine

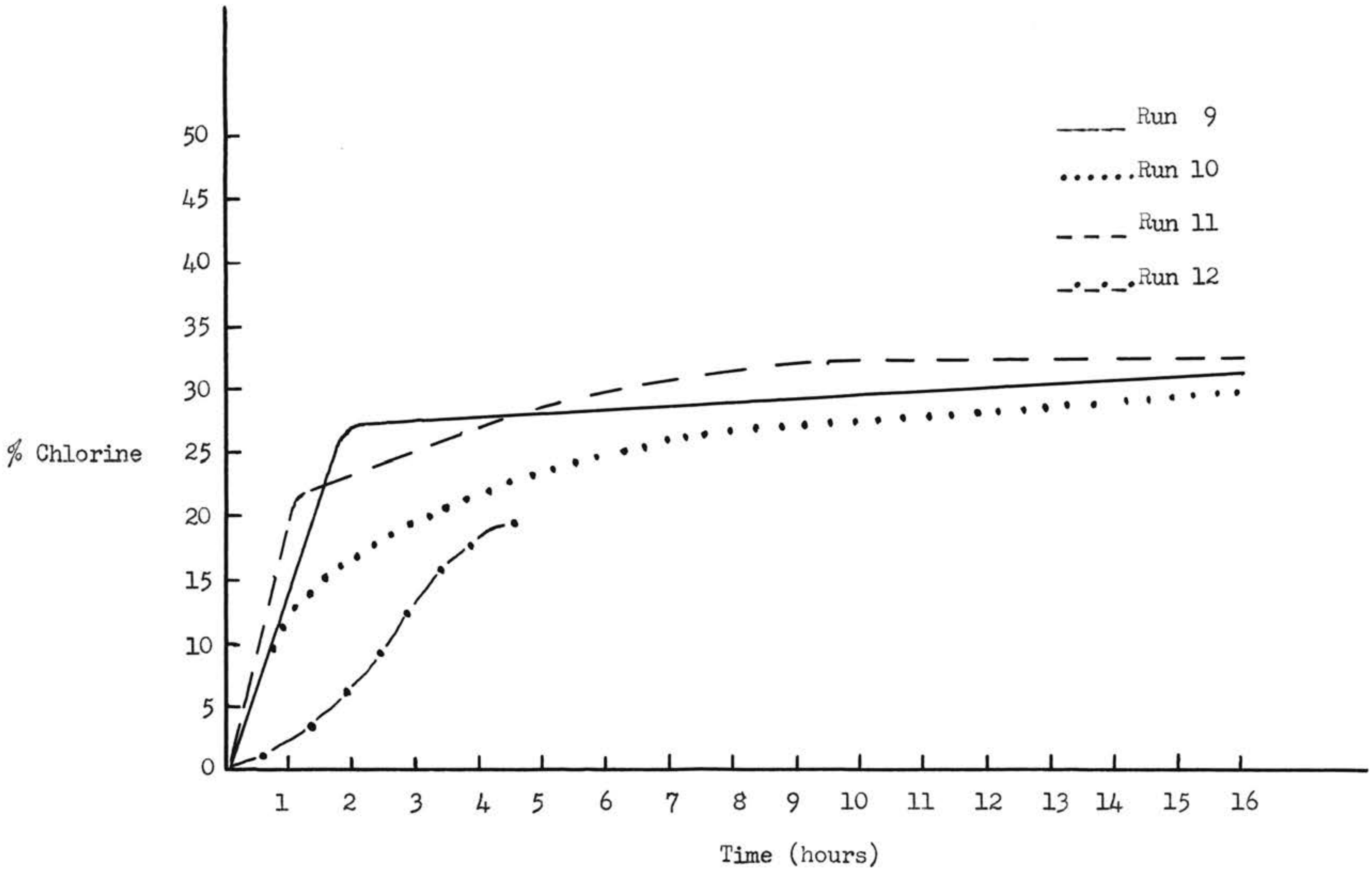

FIGURE 7. RATE OF CHLORINE ABSORPTION

analysis of the periodically removed samples gave the following values with the Fisher Titrimeter: 15.08% to 15.28% at the end of one hour; 26.63% to 27.20% at the end of two hours; 27.36% at the end of three hours; no value at the end of four hours because of loss of the product when the beaker containing it was accidentally knocked to the floor; 26.50% at the end of eight hours; and 30.81% to 31.24% at the end of sixteen hours. The test for hydroxyl groups was negative.

Run 10: Fifty grams of abietic acid were placed in the reaction flask together with fifty milliliters of a saturated solution of chromium chloride and one liter of distilled water. After the solution was cooled to 0° C., chlorine was passed rapidly through the suspension, which was stirred constantly for a sixteen-hour period. Samples were removed from the reaction flask periodically, filtered by suction, washed several times with distilled water, and dried. Analysis for chlorine with the Fisher Titrimeter gave the following values: 16.59% to 16.68% at the end of one hour; 16.95% to 16.98% after two hours; 17.59% to 17.77% at the end of three hours; 21.54% to 21.74% after four hours; 27.08% to 27.35% at the end of eight hours, and 29.89% to 30.35% after sixteen hours. The test for hydroxyl groups on the terminal products was negative.

Run 11: Fifty grams of abietic acid, five tenths of a gram of iodine, and one gram of potassium iodide were placed in the reaction flask. When one liter of distilled water had been added to the mixture and the solution cooled to 0° C., chlorine was passed rapidly through the constantly stirred suspension for sixteen hours. Samples removed from the reaction flask periodically were filtered by suction, washed repeatedly with distilled water, dried, and analyzed for chlorine content. The values obtained with the Fisher Titrimeter were as follows: 17.78% to 17.86% after one hour; 21.74% to 21.97% after two hours; 24.71% after three hours; 25.09% to 25.30% after four hours; 31.02% to 31.08% at the end of eight hours; and 32.00% after sixteen hours. The test for hydroxyl groups on the terminal product was negative.

Run 12: Fifty grams of abietic acid were placed in the reaction flask with fifty milliliters of a saturated solution of nickel chloride and eight hundred milliliters of distilled water. The solution having cooled to 0° C., chlorine was passed through it at a rapid rate with constant stirring for sixteen hours. The chlorine values obtained by the gravimetric method were as follows: 2.98% after one hour; 7.66% after two hours; 13.84% after three hours; and 17.94% after four hours. The analysis could not be completed because of the rapid decomposition of the reaction product.

An attempt was made to crystallize some of the terminal products by first dissolving a quantity of the material in a water-methanol mixture and then cooling the solution in a mixture of dry ice and acetone. This method failed to yield crystals, and no further attempt was made.

The failure of the Borglin method to produce a chlorine-containing compound presented an interesting problem. One reason believed responsible for the failure was that the chlorination products were found to be unstable in the range of temperatures specified for Borglin's method of chlorination. Another possible explanation was the theory that the reaction products may have undergone a coupling reaction with the carbon tetrachloride in the presence of the aluminum chloride, as is known to occur in the Freidel and Crafts type reactions. This was tested by placing several grams of a chlorinated reaction product in a two hundred fifty milliliter Erlenmeyer flask with fifty milliliters of dry carbon tetrachloride and a small amount of aluminum chloride. The solution was warmed slightly in a steam bath and allowed to stand for a few minutes. The mixture began to evolve large amounts of hydrogen chloride almost immediately, and the bottom of the flask became too hot to touch. The mixture in the flask darkened considerably. No attempt was made to recover the products for analysis. Freshly prepared chlorination products as from run twelve did not react as did the older, partially decomposed products as from runs nine, ten, and eleven. This failure may have been caused by the absence of hydrogen chloride, which has been found to be necessary to initiate such reactions.

DISCUSSION

The problem as presented was twofold: to establish on a reproducible basis Bobst's (16) work involving the chlorination of aqueous suspensions of abietic acid; and, in addition, to determine whether a stable chlorine addition product could be prepared. The need for proof that the method could be duplicated was shown by the fact that of the four references cited as methods of preparing chlorination products of abietic acid, not one of them could be reproduced by those working on the problem here at Oklahoma A. and M. College.

The experimental work reported in this paper resulted in chlorination products having chlorine contents near those reported by Bobst. It was concluded from this that his work was reproducible, in contrast to the other methods reported in the literature. The rate of addition of chlorine was found to be dependent on the use of a catalyst. Terminal products in all runs carried out for extended periods (sixteen hours or more) at temperatures near 0° C., however, were found to contain approximately two moles of chlorine, which agrees with the theoretically predicted values. The nature of the catalyst was found to effect only the rate at which the first three atoms of chlorine added to the molecule. It was found that chromium chloride was a more effective catalyst than nickel chloride, and that chromium chloride used together with iodine and potassium iodide gave the most favorable results, as is illustrated by the graph in Figure 7.

No positive evidence could be found as to the existence of a stable chloride addition product. Some of the products prepared appeared to be stable for periods of as long as two and one-half months, but all of the compounds were found to be undergoing decomposition after standing over the summer. The gaseous product of decomposition was, in every case, hydrogen chloride. The instability of these compounds made itself most noticeable when attempts were made to determine their molecular weights and neutralization equivalents. The Beckman freezing point method of molecular weight determinations gave continuously increasing values, starting near the expected values and rising as high as eight hundred with succeeding determinations. The determination of the neutralization equivalents did not reach the same extremes as the molecular weights, but values did occur that were half again as large as the expected values. For this reason, the method was discarded as a means of estimating the molecular weight of the compound, and the values obtained were used only as a means of ascertaining the presence of the carboxyl groups in the molecule.

The ferric hydroxamate test for hydroxyl groups was found to give positive results for reaction products containing less than 26% chlorine but negative results for reaction products containing more than 26% chlorine, regardless of the catalyst used. It had been thought at first that the chlorination had taken place through the addition of hypochlorous acid, forming a chlorohydrin; but the fact that it was possible to obtain a compound that contained two moles of chlorine suggested that a direct addition of elemental chlorine had taken place. Although no evidence could be found to indicate that the chlorine had substituted into the isopropyl side chain of the acid, if a substitution of tertiary hydrogen by chlorine had taken place, the chlorine could be readily hydrolyzed in aqueous solution with the evolution of hydrogen chloride and the replacement of the chlorine by a hydroxyl group. This theory might serve as an explanation for the positive hydroxyl test.

No correlation could be made between the type of catalyst and the presence of hydroxyl groups or between the presence of hydroxyl groups and the stability of the compound.

When the chlorination products were completely dehydrohalogenated with strong potassium hydroxide solution and then hydrolyzed in an acid solution, a compound resulted which decolorized potassium permanganate. This was taken as an indication that the olefinic character of the molecule had been regenerated.

The fact that the partially decomposed reaction products were found to react with a mixture of dry carbon tetrachloride and aluminum chloride deserves further study for the purpose of attempting to identify the resulting products. It would be of interest to know if other halogen containing solvents yield the same results.

One important problem which remains to be solved is the development of a method for the purification of the chlorination products by low temperature crystallization, chromatographic separation, or extraction. Although the chlorination product is known to be a complex mixture of isomers rather than a pure substance, until a pure product is obtained the material cannot be accurately characterized.

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