THE REACTION OF SODIUM ON ACETIC ANHYDRIDE

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By

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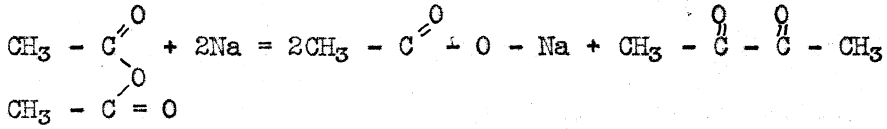
INTRODUCTION

The purpose of this research was that of studying the reaction between sodium and acetic anhydride. This reaction was carried out at room temperature and at high temperatures in order that comparison might be made between the products obtained at each temperature.

An effort was made to determine the mechanism by which the reaction occurred. Data was obtained from observation of the reactions from the identity of the products from the amounts obtained after reaction was complete.

The theoretical reaction may be represented by the equation:



That this equation does not account for the complete reaction was indicated by the fact that diacetyl was not isolated from the products of the runs. The fact that a resin, possibly resulting from polymerization of diacetyl, was formed is also important.

HISTORY

The literature gives little information concerning the reaction of sodium on acetic anhydride. This reaction was studied by Suknevich and Levkin.[1]

They placed 500 cc. of freshly distilled acetic anhydride in a flask equipped with a reflux condensor. They then added in small portions a total of 20 gm. of sodium through a side arm. The flask was heated and allowed to react at the boiling temperature. Reaction products reported were hydrogen, ethylidene diacetate, vinyl acetate, diacetyl and resin.

The authors stated that the above reaction proceeded very slowly, if at all, when carried out at room temperature. The value of these experiments was limited by the failure of the workers to protect the system from atmosphere.

Further work in this field was done by G.D. Kyker[2]. He modified the technique of Suknevich and Levkin and reported somewhat different results. Kyker placed acetic anhydride in a round-bottom flask and sodium in a Soxhlet extractor above. The system was closed to the outside air and swept by a current of inert pyrofax gas. At 137° the acetic anhydride vapors passed up through the extractor and reacted with sodium. The products reported by Kyker were sodium acetate, diacetyl and a resinous material. This resin was believed by Kyker to be a polymerization product of diacetyl.

1. Suknevich, J.F. and Levkin, N.F.; J. Gen. Chem.(U.S.S.R.), 7,857 1937.
2. Kyker, G.D., Unpublished Thesis, 1941.

Kyker's work was repeated by E.U. Elam.[1]

Elam placed metallic sodium and acetic anhydride in a single chamber, closed to outside atmosphere. The flask was heated to 137° and kept at that temperature for half an hour. Elam reported sodium acetate, diacetyl and resin as products of the reaction.

1. Elam, E.U., Unpublished Thesis, 1942.

EXPERIMENTAL

In this study of the reaction of acetic anhydride and sodium two general procedures were used. The high temperature reactions were carried out at 100° and also at the boilint point of acetic anhydride (137°). The system was closed to the atmosphere and swept by a current of pyrofax gas.

Reactions were also carried out at room temperature in erlenmeyer flasks equipped with drying tubes.

Materials:

1. Acetic Anhydride

The acetic anhydride used in this work was from Coleman and Bell and had a purity of 95%. This was placed over P_2O_5 and allowed to stand for 24 hrs. with frequent shaking. The liquid was decanted and distilled at ordinary pressure. The distillate (B.P. 137°C) was placed over pure metallic sodium which retained its luster after 24 hrs. showing the anhydride to be free from impurities.

2. Sodium

Metallic sodium was removed from paraffin oil and cut into small blocks. The blocks were freed from crust and washed with absolute ether. They were then placed in the liquid to be purified and allowed to stay at least 24 hrs.

When used in the reaction with acetic anhydride, sodium was treated as described above. It was then weighed on rough balances under xylene and placed under 150 cc. of xylene in a round-bottom flask. The flask was equipped with a reflux condensor and heated until the sodium was melted. The flask was removed and allowed to cool slightly. The contents were stirred vigorously with a flattened glass rod. This caused the sodium to

break up into very small globules which remained separated after cooling to room temperature. The sodium and xylene were poured into an evaporating dish where the xylene was decanted from the birdshot sodium. The sodium was washed several times with anhydrous ether, after which the metal retained its luster.

3. Anhydrous Ether

Ethyl ether, grade U.S.P. was distilled on a water bath to separate it from high-boiling impurities. The distillate was placed in an erlenmeyer flask with calcium chloride. After 24 hours the ether was distilled and placed over P_2O_5 where it remained for 24 hours. The distillate was placed over sodium until needed as a wash liquid or as a solvent.

4. Toluene

Toluene was used as a solvent and as a diluent in high temperature runs. It was distilled and placed over metallic sodium until needed.

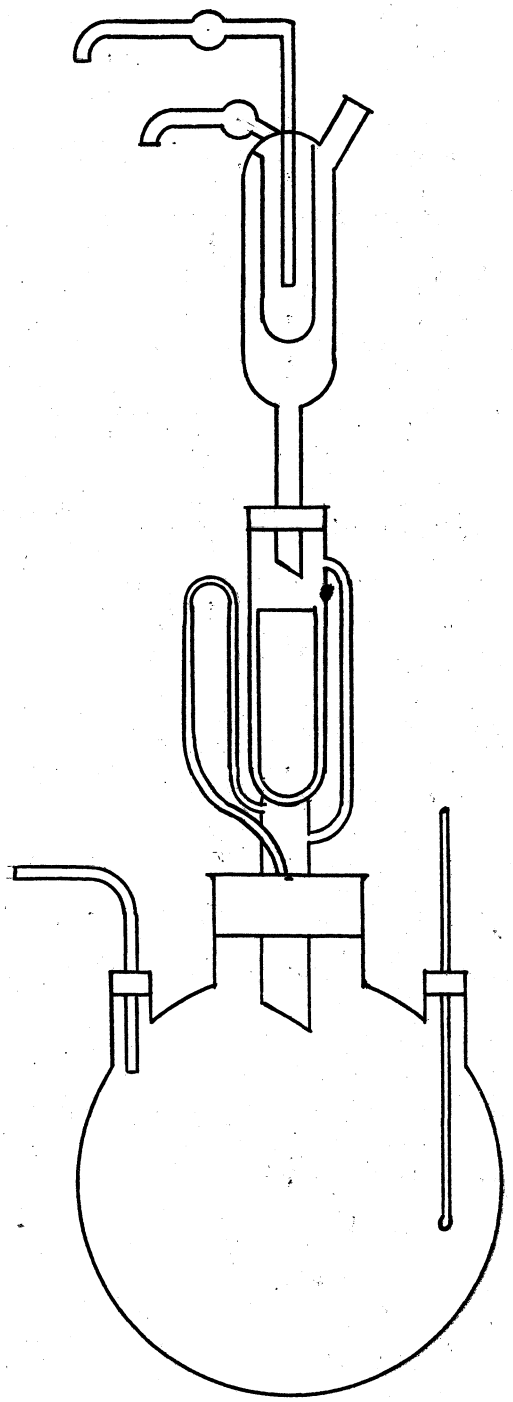
5. Pyrofax Gas

Pyrofax gas was used to provide an inert atmosphere for high temperature runs. It was piped directly from the gas line. The gas contained 98% propane and 2% butane, according to the manufacturers. It was passed through a glass tower containing 50% NaOH which removed any CO_2 present. It was then passed through a tower containing concentrated H_2SO_4 which removed moisture. The gas was then passed directly into the reaction chamber through an opening in the flask.

Apparatus

The reaction at high temperature between sodium and acetic anhydride took place in a three-neck round-bottom flask of 1000 cc. capacity. Inert gas was let in through one small opening, the other being equipped

with a thermometer. A reflux condensor extended down through the middle of the flask. The top of the condensor was connected to a gas line leading through a window to the ground. This allowed free passage of pyrofax gas through the system at all times.



APPARATUS FOR HIGH TEMPERATURE RUNS

HIGH TEMPERATURE RUNS

PROCEDURE

In studying the high temperature reactions between sodium and acetic anhydride two purposes were kept in mind. The first aim of this project was that of determining the best mode of procedure for carrying out the reactions. The second objective was the isolation and identification of the products obtained. It was hoped that a method for obtaining quantitative results might be worked out upon completion of the research.

Five high temperature runs were made, improvements being added wherever possible.

For the first run a Soxhlet extractor was placed between the reaction chamber and the condensor described under "Apparatus". In the reaction flask 250 cc. of pure acetic anhydride was placed. About 10 gm. of "birdshot" sodium, prepared as previously described, was placed in the extractor. Glass wool and glass beads were placed in the extractor to permit free passage of acetic anhydride over the sodium.

A hotplate was placed under the flask and heat was applied. During the reaction pyrofax gas was passed through the system.

At 137° acetic anhydride vapors passed up into the extractor where reaction with the sodium occurred. The sodium acquired a covering of white crystals, and a brown substance was formed in the extractor. This colored material was carried down into the reaction chamber to be dissolved in acetic anhydride. After half an hour heating was stopped and the system allowed to cool.

All material in the reaction flask was rinsed out with acetic anhydride and placed in an erlenmeyer flask for purification.

There remained in the Soxhlet extractor a mass of crystalline material along with some of the brown substance formed during the reaction. The extractor was connected to a 500 cc. round-bottom flask containing 200 cc. of pure ligroin. Heat (100-110°C) was applied and the reaction product extracted with ligroin. Most of the colored material was dissolved in the ligroin, being carried down with a small amount of the crystalline compound. At the end of this extraction about 10 cc. of acetic anhydride, carried down from the crystalline mass, was found. This was immiscible with ligroin and was removed by means of a separatory funnel. The acetic anhydride was added to the original acetic anhydride from the reaction flask. The ligroin solution was bottled for purification. The crystalline solid was dissolved in water for analysis.

In the second run a Soxhlet extractor was not used, 11.5 gm. of sodium and 250 cc. of acetic anhydride were placed in the reaction chamber previously described. The flask was heated to 137°, the boiling point of acetic anhydride. Below 100° no reaction occurred. When the temperature reached 100° the reaction proceeded rapidly with explosive violence. Some of the material in the flask was lost, but the system was closed again and heating continued. After this the reaction proceeded slowly. After half an hour heating was stopped and the flask allowed to cool.

The material in the flask was extracted with acetic anhydride, benzene, ether and water in that order. Each fraction was bottled for tests.

The third run was carried out as described for Run No.2. A water bath was used to prevent explosion. This measure did not prove effective for

some of the material was lost. Extraction was carried out as in Run No.2.

Runs 4 and 5 were carried out as before with modifications. Instead of acetic anhydride, 200 cc. of pure toluene was placed in the flask to decrease the violence of the reaction. In Run No.4, 11.7 gm. of sodium was used, 15.4 gm. being used in Run No.5. The sodium was placed in the toluene which was then heated to 100° on a water bath.

The opening in the flask formerly used for a thermometer was equipped with a dropping funnel containing 200 cc. of acetic anhydride. The anhydride was passed into the reaction chamber, at a rate of three drops per second. The rate was increased as reaction proceeded. This method gave the best results of any of the methods used. The reaction proceeded slowly and evenly. The time required was about 45 minutes.

The flask was allowed to cool and its contents filtered on a Buchner funnel. The crystalline product was washed with acetic anhydride until white. Acetic anhydride remaining on the filter was removed by repeated extraction with ether. The solid was dissolved in water and made up to one liter for analysis.

The filtrate was a deep red solution containing acetic anhydride, toluene and dissolved reaction products. Purification of the products will be described under results.

RESULTS

The three main products sought in the high-temperature runs were sodium acetate, diacetyl and resin.

Sodium Acetate

The crystalline solid formed in the high temperature runs was proven to be sodium acetate. The liquid fractions described for the first three runs were extracted with water, except for acetic anhydride which was miscible with water. Acetic anhydride fractions were distilled to remove the solvent and leave behind a crystalline solid colored brown by a resinous product. The residue was dissolved in distilled water.

In each of the first three runs the water solution was decolorized with charcoal. The solid was recrystallized from hot water and dried. Flame tests were made on the solid. Sodium was indicated by a bright yellow flame. A precipitate was formed when crystals were dissolved in water and magnesium uranium acetate was added. This was a positive test for sodium.

Acetate ion was tested for with lanthanum nitrate solution. A deep blue color indicated that acetates were present. $FeCl_3$ solution gave a reddish-brown precipitate when several of the crystals were added. This was a positive test for acetate ion. The crystals were dissolved in water and H_2SO_4 added. When the solution was heated the characteristic odor of acetic acid could be detected.

In the first three runs only qualitative results were obtained. A method for the quantitative recovery of the products had not been worked out. In the second and third runs the reaction resulted in an explosion. This caused loss of material.

The sodium acetate obtained from each of the fourth and fifth runs was dissolved in water and diluted to exactly 1000 ml. From each solution three 10 cc. aliquots were taken for determination of the sodium acetate. Each aliquot was placed in a distilling flask with excess 85% H_3PO_4 and heated. All liquid distilling over below 170° was caught in an erlenmeyer flask. The acetic acid thus liberated was titrated with .127 N NaOH and the weight of sodium entering the reaction calculated.

In Run No.4 the calculated weight of sodium obtained was 10.5 gm,, 10.6 gm., and 10.6 gm. Three check runs were made. 11.2 gm. of sodium was the amount weighed out for the reaction. The difference in weights was due to losses in purification of the metal.

In Run No.5 the amount of sodium weighed out for the reaction was 15.5 gm. The weights of sodium calculated from experimental data were 15.2, 15.2, and 15.3gm.

Diacetyl

The liquid fractions described under procedure were distilled and the distillation temperatures carefully noted. Diacetyl was described by the handbooks as a greenish-yellow liquid distilling over at 88°C. In no case was a liquid distilling at a temperature near 88° observed to come over. The distillate in all cases was clear, and tests for diacetyl were negative. These tests will be described in the section dealing with resin.

It is unlikely that the diacetyl was changed by the treatment of the reaction products. This will be explained in connection with the room temperature runs. It must be concluded, therefore, that no diacetyl was present in the products of the high temperature runs.

Resin

Aside from small amounts of sodium acetate, which was not completely isolated in the first three runs, the only residue left on distillation was a brown semi-solid resin. Tests made on the resinous products obtained from the five runs were identical in their results. Extraction of the resin by means of organic solvents did not separate the resin into two or more components. The same substance was obtained from all fractions. Xylene, toluene, ligroin, ether, alcohol, chloroform, carbon tetrachloride, and benzene were tried without success.

In Runs 4 and 5 the resin was recovered quantitatively from the products. The fourth run yielded 9.8522 gm. of resin. From the fifth run 13.1968 gm. of resin was obtained.

Results of the qualitative tests made on the resin are given below.

The resin did not have a sharp melting point. Above 190°C it decomposed.

Classification tests were made to determine solubility and reacting groups present. Procedures for these tests were found in the laboratory text by Shriner and Fuson.[1]

The resin was found to be soluble in alcohol, ether, acetone, acetic anhydride, ligroin, xylene, toluene, benzene and most organic solvents. It was insoluble in dilute acid, dilute base, and 85% H_3PO_4.

1. Shriner and Fuson, Identification of Organic Compounds, Wiley, N.Y., Second edition, 4-75 (1940).

The following classification reagents were used on the resin:

1. Bromine in CCl_4 solution: This test gave negative results. No decolorization of the bromine was observed. This indicated an absence of double-bonded structure.

2. $KMnO_4$: Permanganate solution oxidized the resin quite readily. This indicated double bond structure or the presence of easily oxidized groups.

3. Ceric Nitrate: This reagent did not produce the color change from yellow to red given as a positive test. This indicated an absence of hydroxyl groups.

4. Hydrochloric acid: Zinc chloride solution: Negative results showed an absence of hydroxyl groups.

5. Periodic acid: When this reagent was added a white precipitate appeared, indicating the presence of an alpha-hydroxy acid, or a 1,2-diketone.

6. Sodium Bisulfite: No bisulfite addition product was formed. This showed that no aldehyde group was present.

7. Phenylhydrazine: This reagent gave a heavy brown precipitate after reacting with the resin. This indicated the presence of an aldehyde.

The resin was treated with $KMnO_4$ in a distilling flask and heated. Diacetyl distilled over. The liquid gave a boiling point of 88°/760 mm. on correction. A positive test with creatine showed the liquid to be diacetyl. A red color with creatine is almost specific for diacetyl.

The resin, itself, when refluxed with diacetyl gave a positive test.

The iodoform test gave negative results.

ROOM TEMPERATURE RUNS

Procedure:

For each of the five room temperature runs birdshot sodium was placed with an excess of acetic anhydride in a 500 cc. erlenmeyer flask. The flask was stoppered and equipped with a drying tube then allowed to stand until reaction had proceeded far enough for analysis of the products. The starting date for each reaction was recorded. If the reaction went to completion the date of completion was also recorded.

The contents of the flask remained unchanged for several days after the beginning of the reaction. Then the sodium acquired a coating of white crystalline solid. The liquid in the flask acquired a straw yellow color.

After sufficient time had passed for the reaction in the flask to reach completion (approximately 230 days) or to approach completion the contents were placed on a Buchner funnel and filtered. The crystalline solid on the filter was rinsed with acetic anhydride to remove any colored product. Rinsings were added to the original filtrate. After extraction with acetic anhydride the solid was washed four times with absolute ether ro remove acetic anhydride and give pure crystals.

The solid was dissolved in enough water in a volumetric flask to make a liter of solution. Qliquots of 10 cc. were treated with 85% H_3PO_4 and distilled to determine the acetic acid liberated. The distillation products were titrated with standard base. From the results obtained the amount of metallic sodium entering the reaction was calculated. This procedure was described in the discussion of the high temperature runs.

The filtrate from the reaction flask was carefully neutralized to remove acetic anhydride. Sodium carbonate was used. Neutralization was

found to be necessary. A separate room temperature run was made for the sole purpose of determining the best procedure for separating the products. It was found that where acetic anhydride was present the colored material underwent further reaction if heat was applied. Distillation was considered inadvisable when acetic anhydride was present.

After neutralization the filtrate was saturated with salt and extracted with four 50 cc. portions of absolute ether. The ether fraction was distilled at ordinary pressure on a water bath. The residue, which did not exceed 2 cc. was bottled. The handbooks listed diacetyl as being very soluble in ether and only moderately soluble in water. For this reason, the above method was used to remove any diacetyl present in the water solution and obtain it in a nearly pure state.

The first step in purification of the water-soluble reaction product was removal of all dissolved salts. This was accomplished by vacuum distillation of the water fraction at 20 mm. pressure. The distillate was tested for diacetyl with negative results. Residue consisted of salts and a small amount of resinous material. This residue was extracted with acetone which removed all colored material, leaving behind pure salt crystals. The acetone solution was distilled at 20 mm. to remove any liquid other than acetone. The residue, consisting only of resin, was redissolved in pure acetone. The solution was placed in a weighed sample bottle and evaporated. The bottle with resin was weighed and the weight of the resin obtained by difference.

TABLE I

HIGH TEMPERATURE RUNS

NUMBER	SODIUM USED	REACTION TEMPERATURE	REACTION TIME	DIACETYL YIELD	RESIN YIELD
1	6.9 gm.	137°C	30 Min.	0	
2	11.5	137°	30	0	
3	11.1	100°	40	0	
4	10.6	100°	45	0	9.8
5	15.2	100°	45	0	13.2

TABLE II

ROOM TEMPERATURE RUNS

NUMBER	SODIUM USED	REACTION TEMPERATURE	REACTION TIME	DIACETYL YIELD	RESIN YIELD
1	9.10 gm.	Room	231 days	0	.69
2	15.05	"	237	0	1.27
3	11.11	"		0	.56
4	9.24	"		0	.48
5	10.15	"		0	.74

THEORETICAL DISCUSSION

On the basis of available information the exact mechanism of the reaction between sodium and acetic anhydride cannot be clearly defined. However, there is sufficient experimental data to give a basis for a possible explanation of the reaction mechanism.

It was noted that when the reaction was carried out at room temperature several days passed before appreciable change in the appearance of the reactants could be observed. In the high temperature runs no reaction occurred below a temperature of 95°C. This would indicate that the reactants went through a passive state when first placed in contact with each other. If the temperature remained below 30°C the passive state lasted for at least three days. When the temperature was raised to 95° or above the reaction was sudden and almost spontaneous. Once it was started, reaction proceeded rapidly even though the heat was removed.

The products expected were sodium acetate, diacetyl and resin. Sodium acetate and resin were the only products isolated, either at room temperature or at temperatures above 95°. In no case was diacetyl obtained as a direct product of the action of sodium on acetic anhydride.

The probable course of the reaction is represented by the equations below:

$$\begin{matrix} CH_3 - C = O \\ \quad\quad\ O \\ CH_3 - C = O \end{matrix} + Na = CH_3 - C(=O) - O\text{-}Na + CH_3 - C(=O)-$$

$$2CH_3 - C(=O)- = CH_3 - C(=O) - C(=O) - CH_3$$

$$X(CH_3 - C(=O) - C(=O) - CH_3) = (CH_3 - C(=O) - C(=O) - CH_3)X$$

Intermediate formation of diacetyl was indicated by the appearance of the reaction mixtures at various times. In the high temperature runs a yellow color appeared early in the reaction. Soon afterward the yellow color of the liquid changed to orange and then to deep brown. Diacetyl in solution gives a pale yellow-green color. Resin gives a brown color. This change in color could not be taken as conclusive evidence. It did indicate, however, that an intermediate step occurred during the reaction. The intermediate compound, as indicated by the properties of the resinous product, was probably diacetyl. Assuming this to be possible, it is likely that the resin was formed by reaction between two or more diacetyl molecules to give a condensation product or a polymer.

In the two groups of runs made during this project an acid medium was used. The literature did not give a reference to polymerization of diacetyl in an acid medium. Lang[1] gave a possible mechanism for the interaction of diacetyl molecules in a basic solution.

He reported the formation of dimethyl quinogen when diacetyl was heated in alkaline solution. This compound was the result of a reaction between two molecules of diacetyl. The formula assigned to this compound was as follows:

$$CH_3 - CO - \underset{\displaystyle CH_3}{\overset{\displaystyle /}{C}} = CH - CO - CO - CH_3$$

Polymerization or condensation of diacetyl in an acid medium might

1. Konrad Lang, Z. Physiol. Chem. 208,273 (1932).

take place in a similar manner. The tests made on the resin gave results quite similar to those reported for diacetyl by previous workers. The tests made on the resin in this project have been described. A positive test with creatine indicated a 1,2-diketone structure.

The possibility of the resins' formation from diacetyl raises a question regarding the manner in which the individual molecules combined to form the more complex compound. A clue concerning the structure of the resin may be found in the fact that it was oxidized by $KMnO_4$ to give diacetyl as the product.

Oxidation of most organic compounds by permanganate may be represented by the following reactions:

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3(O)$$

$$H_2O + -C{=}C- + (O) = HO - C - C - OH$$

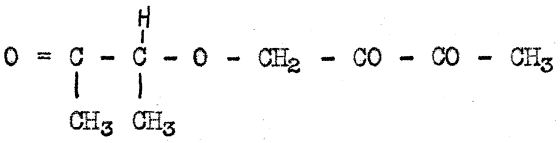
$$HO - C - C - OH + O \rightarrow \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - + H_2O$$

Two explanations may be given to explain the formation of diacetyl by oxidation of the resin. One possibility is that a double bond was broken. This could hardly have been the case since all reagents used to test for multiple bond structure gave negative results.

The presence of one or more hydroxyl groups in the resin molecule gives another possible mechanism for the oxidation of the molecule to give diacetyl. Most of the reagents used in testing for hydroxyl groups did not give definitely positive results. It is not unlikely, however, that one or more hydrogen atoms in the molecule may have migrated to form hydroxyl groups. The existence of these hydroxyl radicals would probably be too

short to give a positive test. But, in the presence of $KMnO_4$ they could easily provide a means by which diacetyl might be formed.

Von Peckmann[1] reported that diacetyl reacted in an alkaline medium to give a compound bearing the following formula:



The results obtained in the present work indicate that the resin obtained should have a structure similar to that reported by Von Peckmann.

1. Von Peckmann, Ber., 21, 1418 (1888).

SUGGESTIONS

1. In the formation of the resin found in the reaction products described previously it is logical to assume that diacetyl is an intermediate product. Some method should be devised to remove the diacetyl from the reaction chamber as soon as it is formed.

2. An attempt should be made to decrease the time required for the room temperature reaction.

3. New solvents should be tried for the separation of reaction products.

4. Further study should be made for the purpose of identifying the resinous product.

SUMMARY

1. Improved methods for carrying out the reaction between sodium and acetic anhydride have been presented. Separation of reaction products and quantitative determination have been made easier by means of the improvements.

2. The only products isolated from either room-temperature or high-temperature runs have been sodium acetate and a resinous material believed to be a polymer of diacetyl. No diacetyl has been isolated from the original products of any reaction.

3. Comparison has been made between reactions at room temperature and runs made at high temperatures. Room temperature reactions have been found to give the same products as high-temperature runs but in much smaller amounts.

4. Theoretical discussion of the reaction is presented. A possible mechanism for formation of the resin are proposed.

5. Suggestions for future study of the problem are given.