A STUDY OF THE SYNTHESIS
OF SODIUM CARBONYL

BY

WILLIAM J. MITCHELL

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE

From the
Massachusetts Institute of Technology
1953

Signature of Author William J. Mitchell
William J. Mitchell

Signature of Professor
Supervising Research Harold S. Mickley
Harold S. Mickley
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Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

May 22, 1953

Professor Earl B. Millard
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

This thesis entitled "A Study of the Synthesis of Sodium Carbonyl" is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

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TABLE OF CONTENTS

I. SUMMARY

Carbon monoxide is reported in the literature to react with molten potassium metal, giving a dark crystalline compound, potassium carbonyl, $C_6(OK)_6$. Upon treatment with alcohol or acids, this compound forms hexaphenol, $C_6(OH)_6$, which is the starting point for many organic compounds.

Sodium is chemically very similar to potassium but no mention of sodium carbonyl is made in the literature. The objectives of this thesis were to reproduce the reported synthesis of potassium carbonyl, and to go on and study the reaction using sodium.

The potassium reaction is reported to have an induction period which goes to almost zero at 220°C.

Hexaphenol reacts with acetic anhydride to form hexaacetoxybenzene, and with the air to form dark red quinones.

One to two gram samples of the metal were washed free from oil and placed in either a stainless steel or glass reactor. The reactor was placed in an oil bath maintained at temperatures of between 170 and 220°C. Dry carbon monoxide was bubbled through the metal for periods ranging from 10 to 550 minutes. It was observed that a dark grey film formed on the surface of the molten potassium, but not on the sodium.

Ethanol was added, giving a small a small amount of grey noncrystalline unfilterable precipitate in the case of the potassium, but not the sodium. This precipitate formed a different type of precipitate when treated with acetic anhydride. This was also nonfilterable and not crystalline. The grey precipitate and the

alcoholic solution of the potassium reaction turned to a dark red when left standing in the air. The sodium solution was unchanged.

From these results, it was concluded that a minute amount of product formed in the potassium reaction; that none formed in the sodium reaction, and that these results have little or no applicability to other reaction conditions.

The reason that the synthesis did not proceed as far as is recorded in the literature is unknown. Possible explanations are offered, assuming either a two phase reaction, or a free radical mechanism.

It is recommended that research be continued on this synthesis; that the effects of pressure, temperature, and radiant energy be studied. It is further recommended that an investigation be made into the possibility of forming hexaphenol as a byproduct in the manufacture of sodium or potassium ethoxide. The metal could be reacted with carbon monoxide, and the resulting carbonyl treated with ethanol, forming hexaphenol and the ethoxide.

II. INTRODUCTION

Early in the nineteenth century, elemental potassium was prepared by reduction of the carbonate with charcoal.

$$K_2CO_3 + 2C = 2K + 3CO$$

Occasionally an undesired explosive byproduct appeared. This substance was later synthesized by duplicating the conditions present in the manufacture. Hot carbon monoxide was passed over molten potassium. The compound was named potassium carbonyl, and its formula was determined to be $C_6(OK)_6$. The reaction for the formation is as follows.

$$6K + 6CO =$$

Upon treatment with hydrochloric acid, water or alcohol, this compound forms hexaphenol, $C_6(OH)_6$. Hexaphenol is an important intermediate in the synthesis of many organic compounds such as rhodizonic acid, inositol, and tetrahydroxy p quinone. If the carbonyl compound could be made cheaply enough, it would have commercial possibilities.

Sodium is chemically very similar to potassium. Therefore it might be expected that a carbonyl of sodium exists also. Since sodium costs roughly one-tenth as much as potassium, a carbonyl of sodium would have better commercial possibilities than potassium carbonyl.

The potassium compound has been reported by several experimenters in the past; however, an extensive search of the literature has disclosed no mention of the sodium compound.

The reaction resulting in the formation of the potassium carbonyl was described by Brodie as follows (3). At first the carbon monoxide is slowly absorbed by the potassium. Greenish grey crystals gradually form on the surface of the potassium, and upon the surface of the surrounding reactor. (These crystals were later determined to be unstable). A second phase of the reaction soon occurs in which the carbon monoxide is strongly absorbed. The final product according to Nietzke and Benckister (9) is a solid that is sometimes bright grey, and at other times reddish brown, green or black.

Neiman and Sushunov reported that the reaction is vapor phase between an evaporated film of potassium and the carbon monoxide. They also determined that the induction period, the period when the carbon monoxide is but slowly absorbed, is a minimum of almost zero at 220°C. It increases rapidly to a "critical temperature" of 290°C above which it is so long that the reaction is halted.

Hexaphenol is reported in the literature as being oxidized by the air to dark orange or red quinones (6). It reacts with acetic anhydride to give hexaacetoxybenzene, which can be crystallized from glacial acetic acid, and is stable in the air (1). Consequently the percent of conversion of a given sample of metal could be determined by forming the phenol and converting the phenol to crystalline hexaacetoxybenzene.

The work undertaken here had two objectives. The first was to react carbon monoxide with potassium in order to see if the results reported in the literature could be duplicated. The second was to run the reaction using elemental sodium instead of potassium in order to prepare sodium carbonyl.

III. PROCEDURE

A sample of the metal weighing between one and two grams was cut, washed in hexane and weighed accurately. This sample was placed in a reactor, covered with hexane and the reactor was placed in an oil bath.

The bath was maintained at a temperature of between 170°C and 220°C. This caused the hexane to evaporate leaving pure molten metal. Nitrogen was passed through the system until all air and residual hexane vapor was purged from the system. Then the flow was stopped.

Carbon monoxide, formed by dehydration of formic acid with sulfuric acid, was carefully dried over phosphorous pentoxide, preheated by passing through a coil in the oil bath, and bubbled up through the metal by means of a tube that extended to the bottom of the reactor.

The flow through the alkalai metal lasted from 10 to 550 minutes. At the end of a run the bath was cooled down to room temperature and the reactor was again flushed with nitrogen.

Reagent alcohol was added to form hexaphenol, and the volume of any gas generated was noted. Any precipitate was filtered, or the liquid was decanted off.

The precipitate was treated with acetic anhydride while the solution was allowed to stand in the air.

Ten runs were made in a reactor which was a cylinder of stainless steel, described under apparatus. Three runs were made using potassium in a glass reactor which was a six-inch pyrex test tube covered with screening. One run was made using sodium in the glass reactor.

IV. RESULTS

It was not possible to duplicate entirely the results reported in the literature concerning the reaction of potassium and carbon monoxide.

Preheated carbon monoxide was found to form a black film on the surfact of molten potassium, and occasionally a bit of dark brown material.

When treated with alcohol a large volume of gas was generated, so large that it exceeded the capacity of the gas collecting tube. The resulting solution had a small amount of gray precipitate present. Most of this precipitate dissolved when the solution was heated. This precipitate was not crystalline; and when filtration was attempted on the cold solution, the precipitate was absorbed by the filter paper.

The precipitate was separated by decantation, and treated with acetic anhydride. A new brown precipitate appeared, different than the original precipitate, but also non-crystalline. This precipitate likewise was absorbed by the filter paper.

The paper on which the original precipitate was absorbed turned from an original color of grey to a dark red-orange upon standing in the air.

The decanted alcoholic solution was a light yellow-green. When stored under nitrogen, it did not change color, but when left standing in the air the color changed to a dark orange-red.

When preheated carbon monoxide was bubbled through molten sodium, no reaction occurred, no black film formed on the surface of the metal, no grey precipitate was present in the alcoholic solution, and no color change occurred in this solution.

V. DISCUSSION OF RESULTS

The results show that it was not possible to confirm quantitatively the results reported in the literature concerning the reaction of potassium and carbon monoxide to form potassium carbonyl. However, the quantitative results indicate that a minute quantity of potassium carbonyl formed.

The carbonyl is reported in the literature as being a dark, sometimes grey or black material. It was found that a dark grey material formed on the surface of the potassium during the reaction.

The compound reacted with alcohol and went partly into solution when heated. The literature reports that potassium carbonyl reacts with alcohol to form hexaphenol, which is slightly soluble in cold alcohol.

The cold alcohol solution had a greyish precipitate present in it. Both this precipitate and the solution turned from an original light color to a dark orange-red when left standing in the air, but did not change color when bottled under nitrogen. Hexaphenol is reported to be oxidized by the air to quinones which are dark orange-red in color.

The literature reports a large quantity of crystals formed in the reaction, but only a thin black film was present in the reactor.

The literature reports that when hexaphenol is treated with acetic anhydride, it forms hexaacetoxybenzene. This compound forms as a precipitate and can be crystallized from glacial acetic acid. It was found that the precipitate present in the alcoholic solution reacted with acetic anhydride and formed a precipitate. However, the precipitate was not soluble in glacial acetic acid, acetic anhydride, or water, and was not crystalline, could not be crystallized, and did not have a melting point below 250°C.

These three things, the formation of a grey film and precipitate, the oxidation of the alcoholic solution, and the reaction with acetic anhydride all confirm an assumption that a minute amount of the potassium has reacted with the carbon monoxide to form the carbonyl.

No explanation is offered for the solubility and melting point behavior of the product formed with acetic anhydride.

The reason for the reaction not going as far as is reported in the literature is unknown. Several explanations are possible, but are based upon assumptions rather than facts.

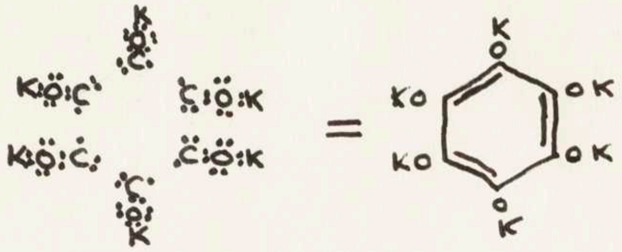
One assumption is that some of the potassium evaporated, and this gaseous potassium was in contact with some carbon monoxide for a longer time than the induction period reported in the literature. This condition should have been reached someplace along the surface of the metal, if not in the passage of a bubble up through the molten metal. A second assumption is that the reaction is vapor phase, which Neiman and Sushunov report.

Many vapor phase reactions have free radical mechanisms, and so a third assumption is that this reaction is of that type. Most free radical reactions such as the chlorination of hydrocarbons are catalyzed by radiant energy. This author would like to postulate the following mechanism for the reaction, assuming that it is catalyzed by radiant energy in the form of light.

$$2K\ (\text{liquid}) = K_2\ (\text{gas})$$

$$K_2 + \text{light} = 2K\cdot$$

$$:C:::\ddot{O}: + K\cdot = :\dot{C}:\underset{\cdot\cdot}{\ddot{O}}:K$$



By postulating the mechanism, and making the assumptions stated above, it is possible to explain many of the phenomena of the reaction.

A few molecules in the reactor would be sufficiently activated to form a minute amount of product without light catalysis, just due to the statistical energy distribution. However, for the reaction to go quantitatively, the presence of a catalyst is evidently necessary.

The mechanism explains the induction period, the period in which the intermediates build up to sufficient concentration to get together in groups of six. It also explains the increase in heat in the second phase of the reaction when the KCO groups combine to form the carbonyl and give off some of their extra energy as heat.

The reaction was run at first in a sealed stainless steel reactor in which no light was admitted. The thermal radiation from the walls of the reactor was evidently not sufficient to make the reaction go quantitatively.

When the glass test tube was used for a reactor, it was wrapped in three layers of screening to prevent any flying glass in case of explosion. The tube was placed well down in the oil bath for good thermal contact, and there was very little chance of any incident light falling on it. This would explain the failure of the reaction to go in the glass reactor.

In the past, the reaction was probably run in at least room light which would catalyze the reaction.

Another explanation can be offered for the failure to reproduce the data of the literature, based on the assumption that the reaction is not vapor phase, but is two phase, between the carbon monoxide and the liquid potassium. The rate of reaction would be limited by the rate of diffusion of the reactants to the reacting interface.

Any contaminant that was present on the interface would inhibit the reaction. It is possible that all of the mineral oil in which the potassium is stored was not washed off. This would leave a thin film of oil on the surface of the metal and effectively slow down the rate of diffusion of the gas to the metal so that the induction period was never exceeded quantitatively, and only a very small amount of the product could form.

Another contaminant of the interface could be elemental carbon or potassium carbonate. This could be formed either by reversal of the reaction of the formation of elemental potassium, or by reversion of carbon monoxide to carbon dioxide and carbon.

$$2K + 3CO = K_2CO_3 + 2C$$

$$2CO = CO_2 + C$$

This carbon film could be the black substance that did not dissolve in alcohol and water. Any such film would adhere to a filter paper and appear to absorb on it. The alcoholic precipitate in the reaction was absorbed by the filter paper.

It was thought that the first ten runs made using the stainless steel reactor were inhibited by the reactor walls. Therefore, the next three runs were made using a glass test tube for a reactor. However, since quantitative results were not obtained in either reactor, it is impossible to say whether any inhibiting effect can be attributed to the steel.

The reaction with sodium showed no tendency to go since there was not even a trace of product formed, and the sodium appeared to be completely unreacted.

An equilibrium expression for this reaction if it were gas phase would involve the product of the fugacities of carbon monoxide and the metal, both raised to the sixth power. At the experimental temperature the vapor pressure of potassium is 2×10^{-2}, while the pressure of sodium is only 5×10^{-4} or one fortieth as much. Since the pressures are so low, the fugacities can be replaced by the vapor pressures. The pressure of sodium to the sixth power would be only about 2.4×10^{-9} as great as that of potassium.

However, the values of the equilibrium constants for both reactions are unknown, and the constant for the sodium reaction need not be of the same order of magnitude as that of the potassium. If it were larger, it would decrease the effect of lower vapor pressure.

Any inhibiting effects that are applicable to the potassium reaction are equally applicable to the sodium reaction.

The experimental run using sodium therefore showed only that under the stated reaction conditions, no product forms. This result has little applicability to different reaction conditions.

VI. CONCLUSIONS

On the basis of the facts of the experimental work, only two conclusions can be drawn.

The first is that under the experimental conditions described, no reaction occurs between sodium and carbon monoxide.

The second is that under the experimental conditions described, it is impossible to duplicate quantitatively the results reported in the literature concerning the reaction of potassium and carbon monoxide. Any product that formed was minute in quantity, non-crystalline, and absorbed on a filtering medium.

VII. RECOMMENDATIONS

It is recommended that work be continued on the synthesis of sodium carbonyl. In order that the results may be more fruitful than these obtained here, it is recommended that the following modifications be made in procedure.

1) That the reactor be made of transparent reinforced glass.

2) That temperature level be controlled by means of either a bath of transparent, heatstable oil, or an oven.

3) That the effect of light of various frequencies be studied.

4) That the effect of various pressures be studied.

5) That the reaction be run as a batch operation rather than the semi-flow method used here. The reactor containing the metal should be evacuated; charged with carbon monoxide, and the rate of the reaction recorded by the fall in pressure. This would eliminate any possibility of the induction period not being exceeded by the gas bubbling through at too rapid a flow rate.

6) That the metal be washed many times with an inert solvent to remove any possible oil film.

7) That a study be made on the purification of sodium or potassium ethoxide formed when ethanol is added to the carbonyl. These ethoxides are now used as catalysts in many base catalyzed condensation reactions. They are prepared by reacting the alkalai metal directly with ethanol. By

reacting the metal first with carbon monoxide and treating the resulting carbonyl with ethanol, it might be possible to obtain a valuable by-product, hexaphenol, at very little additional expense.

VIII. APPENDIX

APPARATUS

The apparatus is shown schematically on Figure I. All letters refer to that figure.

Nitrogen was admitted to the system from a cylinder through a valve (A). A separatory funnel (B) containing formic acid allowed drops to fall on sulfuric acid which was heated on a hotplate in a flask (C). This generated carbon monoxide. A pressure relief line joined the top of the separatory funnel to the main line in order to allow the drops to fall.

Flask (D) is an empty flask provided to prevent any of the potassium hydroxide solution in flask (E) from entering the sulfuric acid.

The carbon monoxide bubbled through the potassium hydroxide and then passed through a large tube packed at (F) with calcium chloride, and at (G) with phosphorous pentoxide.

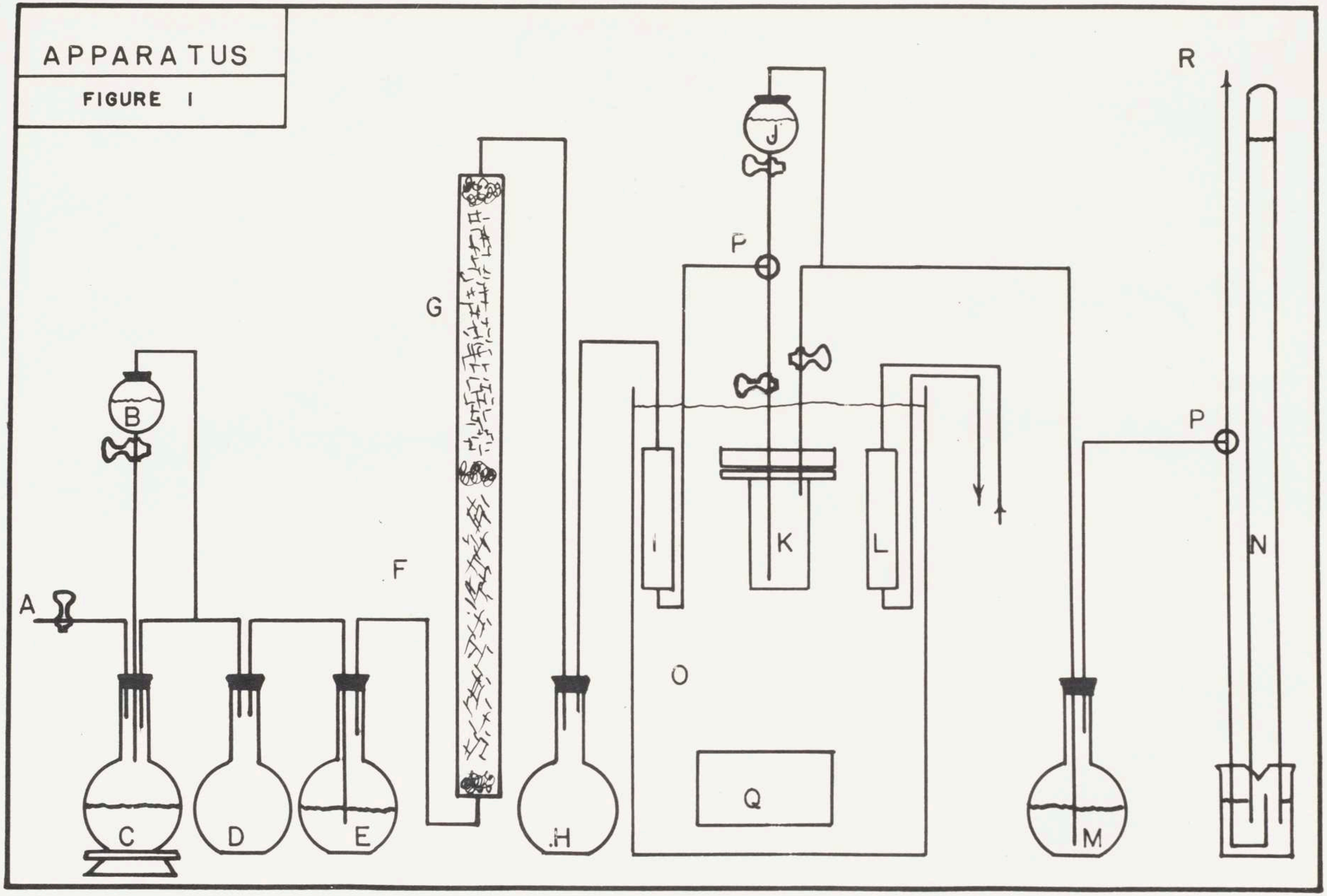
Another trap at (H) is provided to prevent any molten metal from surging back from the reactor and contacting the phosphorous pentoxide.

The gas passed through a preheating coil (I) in oil bath (O), through a three-way valve (P) into the reactor (K) where it bubbled through the molten reacting metal. It then passed through an oil trap (M), a three-way valve (P) and was exhausted out (R) to the hood.

A second separatory funnel (J) was provided for admitting ethanol to the reactor. Both three-way valves were changed when the ethanol was admitted. The valve (J) cut off the first part of

APPARATUS

FIGURE 1



LEGEND FIGURE I

A. Needle valve

B. Separatory funnel containing formic acid

C. 500 ml. flask containing sulfuric acid, on hot plate

D. 200 ml. flask

E. 200 ml. flask containing aqueous potassium hydroxide solution

F. Calcium chloride in a long drying tube

G. Phosphorous pentoxide in drying tube

H. 200 ml. flask

I. Copper coil

J. Separatory funnel containing ethanol

K. Reactor

L. Copper coil through which water flows

M. 200 ml. flask containing mineral oil

N. Gas collecting tube

O. Oil bath

P. Three-way stopcock

Q. Heater thermostat combination

R. Exhaust to hood

the system, and the second directed any gas generated to a collecting tube (N) where the volume could be noted by the volume of water displaced.

The oil bath was heated and maintained at reaction temperature by a heater thermostat combination (Q).

At the completion of a run, the bath was cooled to room temperature by passing water through cooling coil (L).

All tubing used in the apparatus was one quarter inch in diameter, and was fastened together by means of rubber tubing.

The reactor shown in Figure 2 consisted of a stainless steel cylinder threaded on the outside. Screwed onto these threads was a ring of cold rolled steel. Four bolts which bolted on the cover clamp were fastened on to this ring. The cover clamp held a machined stainless steel cover tightly against a machined surface on the top of the reactor. A tight fit was insured by means of a soft copper gasket.

Two one quarter inch stainless steel tubes were silver soldered to the cover. One reached almost to the bottom of the cylinder and was used for admitting the carbon monoxide. The other extended just through the surface of the cover and was the exit for the gases.

Valves were fastened on both tubes so that the reactor could be completely sealed.

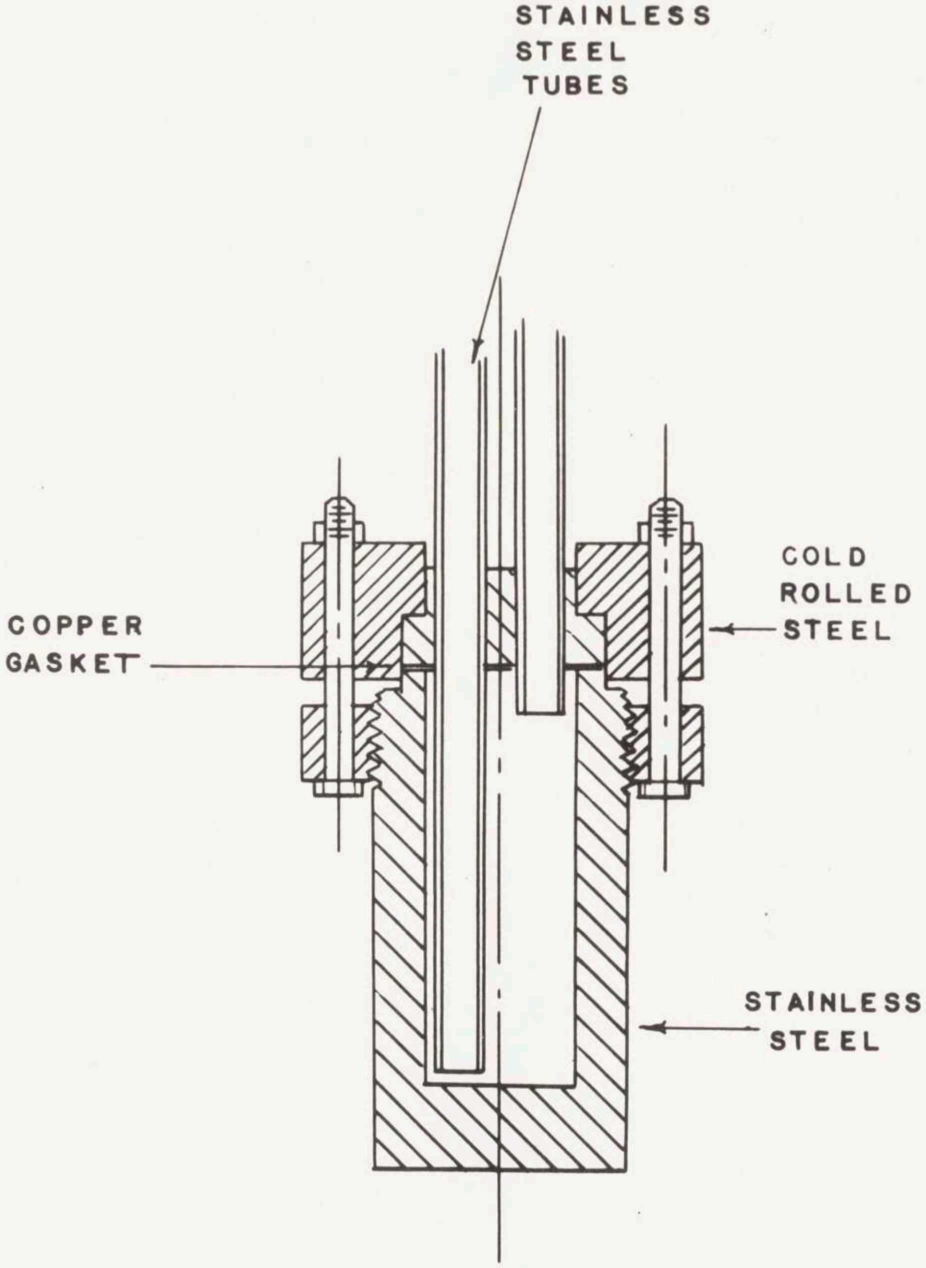
The reactor was made of this heavy steel because it was thought that potassium carbonyl might explode.

The glass reactor was a six-inch pyrex test tube, sealed with a two-hole rubber stopper. Through one hole, a small piece of glass

REACTOR

FIGURE 2

FULL SCALE



tubing extended to the bottom of the test tube, through the other hole a second piece of glass tubing extended about one inch. This was for the entrance and exit of the gas respectively.

Rubber tubing was attached to the outer ends of the glass tubing, and could be sealed by means of pinchclamps.

Protection against explosion was obtained by wrapping the test tube in three layers of wire screening.

The entire system was kept under a hood because of the danger of carbon monoxide leaks. As an added precaution, an ampule for the detection of carbon monoxide was placed at head level outside the hood. This ampule would turn dark if the concentration of carbon monoxide in the room became dangerous. It is manufactured by Mine Safety Appliance Co.

DETAILS OF PROCEDURE

A sample of about one gram of metal was cut, and washed in a hexane fraction of petroleum to free it from any of the heavy mineral oil in which it was stored. The exact weight of the metal was determined on an analytical balance in a weighing bottle half filled with hexane. The metal was then placed in the reactor covered with hexane, and the reactor was sealed.

The heater on the oil bath was started; the bath was brought to the reaction temperature, and kept there by a thermostat. Sulfuric acid in the first flask was heated to about 100°C, and the entire system was flushed out with nitrogen for about 15 minutes.

The reactor was then placed in the oil bath and one valve was opened so that the heated hexane could boil off and be collected in an oil trap. The other valve on the reactor was opened and more nitrogen was passed through until all of the hexane vapor was purged.

The flow of nitrogen was stopped and formic acid was introduced dropwise into the sulfuric acid forming carbon monoxide. A rather large flow rate of this gas was maintained for about five minutes to purge the nitrogen from the system.. This required approximately 5 ml. of formic acid. The flow was then adjusted so that about one bubble per second escaped from the bubbler in the bottom of the potassium hydroxide trap.

Runs were made at temperatures ranging from 170° to 222°C, and lasted from 10 to 550 minutes.

At the end of the run the flow of formic acid was stopped, the heater disconnected, water was circulated through the cooling coils of the bath, and the system was again purged with nitrogen to remove all carbon monoxide. When the bath reached room temperature, the nitrogen was shut off and the three-way stopcocks were changed so that the alcohol could flow into the reactor and any gases generated would flow into the collecting tube.

About 10 ml. of alcohol or acetic anhydride were slowly admitted into the reactor. The effluent gases were collected in the tube until its capacity was reached, and the remaining gases were exhausted to the hood.

At first it was intended to form hexaacetoxybenzene directly in the reactor by the addition of acetic anhydride according to the following reaction.

$$C_6(OK)_6 + (CH_3CO)_2O + H_2O = 2\ HOOCCH_3$$

This was done in runs 1, 2, and 3. However, the anhydride does not react with the residual potassium and difficulty was experienced in destroying the potassium. In order to destroy the metal slowly, an acid had to be formed; so water was added to the reactor.

$$(CH_3CO)_2O + H_2O = 2\ HOOCCH_3$$

$$K + HOOCCH_3 = KOOCCH_3 + 1/2\ H_2$$

However, the potassium reacted preferentially and violently with the free water present, liberating hydrogen, which caught fire, charring the entire contents of the reactor.

As a consequence, in succeeding runs ethanol was admitted to the reactor. This reacts with the carbonyl to form hexahydroxybenzene (hexaphenol) and with the unreacted potassium to form potassium ethoxide. Both reactions proceed at a slower rate.

$$6\ C_6(OK)_6 + 6\ C_2H_5OH = C_6(OH)_6 + 6C_2H_5OK$$

$$K + C_2H_5OH = C_2H_5OK + 1/2\ H_2$$

The contents of the reactor were washed into a beaker. The solution or slurry was then treated by one of the following procedures.

A. The slurry was filtered and the resulting precipitate was treated with hot acetic anhydride. This formed hexaacetoxybenzene from any hexaphenol present, and potassium acetate from any potassium ethoxide or potassium hydroxide present. The anhydride solution was then diluted with water for form an aqueous acetic acid solution. In this cold solution all species present are soluble but the hexaacetoxybenzene. The solution was filtered and the precipitate treated with hot glacial acetic acid to recrystallize the hexaacetate.

B. The slurry was filtered and the alcoholic solution was allowed to stand in the air.

C. Entire reactor contents were evaporated almost to dryness and then treated by the same procedure described in A.

D. Same as B except that crystallization of the hexaphenol was attempted from water, alcohol, and ether.

The material balance was set up in the following manner. Input was determined by direct weighing of the metal. Product was to be determined by two methods. The first of these was by weighing any crystalline product obtained. The second was a method using the volume of gas generated upon addition of alcohol to the reactor. Potassium carbonyl reacts with ethanol by an exchange reaction and does not liberate any gas. The unreacted potassium reacts with the ethanol liberating one half mole of hydrogen for every mole of potassium present. The volume of gas generated would give directly the amount of potassium unreacted.

SUMMARY OF DATA AND OBSERVATIONS

The reaction conditions of the synthesis are listed below for the fourteen runs made.

Run	Temp. °C	Wt. Sample grams ±.002	Reaction Time min. ±2	Reagent added to Reactor
1	198±2	0.265	10	Acetic Anhydride
2	190±10	1.280	38	Acetic Anhydride
3	185±15	0.823	50	Acetic Anhydride
4	180±10	0.509	100	Ethanol
5	200±2	1.405	131	Ethanol
6	199±3	1.093	190	Ethanol
7	220±2	1.738	100	Ethanol
8	220±2	1.254	290	Ethanol
9	205±15	2.112	360	Ethanol
10	222±2	1.212	550	Ethanol
11	201±6	1.141	65	Ethanol
12	222±2	1.141	215	Ethanol
13	222±2	0.963	70	Ethanol
14	222±2	2.951	75	Ethanol

Observations and Procedures:

In runs 1 through 10 all observations begin with a description of the contents of the reactor after the stated reagent was added. In runs 11 through 14 observations begin with a description of the contents of the reactor before any reagent was added.

Run 1.

A very few dark specks were present, and most of the potassium appeared unreacted. Glacial acetic acid and water were added and the resulting mixture was washed into a beaker. There the potassium slowly reacted; the solution became turbid, but no precipitate formed.

Run 2.

A black material was present along with a large amount of unreacted potassium. The gas appeared to have channeled up through the metal. The acetic anhydride solution was diluted and filtered, but the small amount of precipitate present was absorbed by the filter paper.

Run 3.

The material in the reactor looked exactly the same as in run 2. Difficulty was experienced in destroying the unreacted potassium. It reacted violently with the water added as a diluent to the acetic anhydride and the resulting gas caught fire. This charred the contents of the reactor. The charred material was filtered out. No crystals formed from the filtrate.

Run 4.

A reddish green solution resulted with a noticeable amount of grey precipitate. The solution was filtered but the precipitate was not crystalline and was adsorbed by the filter paper. No product resulted.

Run 5.

The resulting solution was pale yellow with a precipitate of white and black particles that were partially soluble in water. The slurry was bottled under nitrogen overnight and did not change color. It was filtered, giving no crystalline product, but leaving a greyish material on the filter paper that slowly turned dark red in the air.

The filtrate was evaporated almost to dryness and a precipitate formed that looked like a gel. This gel was dissolved in ethanol. No crystals could be induced to form. The solution was again evaporated. The precipitate was dissolved in water. Once more no crystals would form. It was evaporated almost to dryness. Ether was added and heated to boiling, but the precipitate would not dissolve.

The ether was boiled off and the precipitate was redissolved in alcohol. It was allowed to stand overnight in the air and the solution turned dark red.

Run 6.

The alcoholic solution was identical with that obtained in run 5. No crystals would precipitate from it.

Run 7.

A considerable quantity of greyish precipitate was present in the alcoholic solution. To a small portion of this material more alcohol was added dissolving most of it, but leaving a small amount of black precipitate.

The alcoholic solution was decanted from most of the original precipitate. Acetic anhydride was added to this precipitate and heated. A vigorous reaction took place with the evolution of a large quantity of gas. The solution was diluted with water, and no precipitate was present. The solution was evaporated to dryness. It turned dark brown. Water was added, giving a brownish solution with a brown non-crystalline precipitate. The liquid was decanted and the precipitate was treated with hot glacial acetic acid. The precipitate was not soluble, and did not melt when heated to 250°C.

The alcoholic solution from the reactor was evaporated almost to dryness, treated with acetic anhydride, and diluted. A brown precipitate formed again, similar to the one above. This precipitate also was not crystalline, could not be filtered, and was not soluble in glacial acetic acid.

Run 8.

A black precipitate was present in the reactor. The contents were evaporated to about 1 ml. Five ml. of acetic anhydride were added. This was diluted with water and filtered. The small amount of precipitate formed adhered to the filter paper. There was no crystalline product.

Run 9.

Results the same as run 8.

Run 10.

Large amount of black precipitate present. This was filtered off and discarded. It looked like carbon black. The solution was a light dirty orange color. Upon standing in air, it turned dark red.

Run 11.

This run was made using conditions similar to those above, but a glass test tube was used instead of the stainless steel reactor. The cold tube was removed from the bath after the run and before any alcohol had been added. The tube had a deposit of solid unreacted potassium on the bottom. The top of the potassium was covered with a black film, while the metal itself seemed almost entirely unreacted.

Ethanol was added and the potassium destroyed. A black precipitate was left that was similar to that found in the runs made using the stainless steel reactor.

The original solution was almost colorless, but turned dark orange upon standing overnight in the air.

Run 12.

This run was also made using the glass reactor. After the carbon monoxide had passed through for two hours, the reactor was sealed off and removed from the oil bath while still hot. White specks were present on the side of the tube. Black and grey particles were present on the bottom floating on a layer of liquid potassium. The tube was replaced in the oil bath and CO was passed through it for one hour more. It was removed again, and observed, but appeared just as before. It was replaced in the oil bath and cooled. Alcohol was added and a large amount of gas was evolved. A precipitate was formed in a pale yellow solution. The solution was decanted and the precipitate treated with acetic anhydride, producing a violent reaction. When the reaction subsided, water was added, and a small amount of unfilterable precipitate was present.

The decanted alcoholic solution turned dark orange after standing overnight.

Run 13.

In this run the apparatus was modified so that the gas went directly into the reactor as soon as it left the preheating coil. The tube was removed from the hot oil bath and examined. On the surface of the molten potassium was a black film that had the appearance of carbon black. A few brownish specks were also present.

The tube was cooled in the bath. Alcohol was added to give a pale yellow solution with a greyish precipitate that was partially soluble in water. Upon standing in air the solution turned dark orange. No crystals could be induced to form.

Run 14. Sodium

This run was made using sodium in a glass test tube. The tube was observed during the course of the runs; no reaction was apparent, and no black film formed on the surface of the molten metal. The tube was cooled, and alcohol was added. There was no precipitate and the solution did not darken upon standing in the air.

LITERATURE SURVEY

In the year 1825 metallic potassium was prepared by the reduction of the carbonate with charcoal according to the following reaction.

$$K_2CO_3 + 2C = 2K + 3CO$$

Occasionally a grey explosive mass appeared as an undesired by-product of this preparation. (8)

In 1834, Justus von Liebig became interested in this reaction. In his laboratory he passed preheated carbon monoxide over elemental potassium, and obtained this dark grey mass. His experimental conditions duplicated those present in the manufacture of the potassium. Hot carbon monoxide was in contact with hot potassium. The product exploded violently upon contact with water, and reacted violently with hydrochloric acid. (6)

In 1860 Brodie repeated this experiment. (3) He described it as follows. At first the carbon monoxide is absorbed slowly by the potassium. Greenish grey crystals gradually form on the surface of the surrounding reactor. (These crystals were later found to be unstable.) A second phase of the reaction soon occurs in which the carbon monoxide is rapidly absorbed, the crystals become dark red, and there is a large evolution of heat. By weighing the reactor before and after the reaction, Brodie determined that one mole of carbon monoxide was absorbed for every gram atom of potassium present. This gave the compound the empirical formula of KCO.

In 1885 Nietzki and Benkister ran the reaction, but under more controlled conditions. (2) They took about five grams of potassium, carefully dried it from petroleum and placed it in a short, rather wide combustion tube. This tube was placed in a sand-filled gutter, and heated with a simple bunsen flame.

In one end dry, CO_2 free, carbon monoxide was admitted. This was collected at the other end in a collecting tube by displacement of mineral oil.

The carbon monoxide displaced the air in the tube, and the potassium was then heated to somewhat over its melting point.

They found that the reaction proceeded rather slowly at first and did not accelerate with further heating. After a while, a green crystalline mass appeared on the surface of the potassium.

A second phase of the reaction began in which the carbon monoxide was absorbed so strongly that it was not possible to maintain an excess bubbling into the gas collecting tube.

The product was a solid that was sometimes bright grey, and other times reddish brown, green, or black. It was found to be difficult to remove from the reactor.

They also reported that if the compound was prepared from completely dry gas, and that if local overheating was eliminated, there was no explosion. They found that the product was not pyrophoric and that the cold reactor could be safely opened in the air, though it would react upon long exposure.

As a result of their experiments, Nietzki and Benkister confirmed the empirical formula of KCO and found that the true formula was $C_6(OK)_6$.

They found that the carbonyl would react slowly with alcohol and go into solution; would react with hydrochloric acid to form hexaphenol, and with acetic acid to form hexaacetoxybenzene.

$$C_6(OK)_6 + 6C_2H_5OH = C_6(OH)_6 + 6C_2H_5OK$$

$$C_6(OK)_6 + 6HCl = C_6(OH)_6 + 6KCl$$

$$C_6(OK)_6 + 6(CH_3CO)_2O = C_6(OOCCH_3)_6 + 6CH_3COOK$$

In 1950 Neïman and Sushunov ran a series of reactions to determine the nature of the induction period of the carbonyl formation. (8) The induction period is the period when the carbon monoxide is slowly absorbed. They found that at a pressure of 10 mm. of mercury, the induction period was a minimum of almost zero at 220°C. and that it increased rapidly to a "critical temperature" of 290°C. Above this temperature, it was so long that the reaction was practically halted. They also concluded that the reaction was vapor phase between carbon monoxide and an evaporated film of potassium.

Below 170°C the main product of the reaction between carbon monoxide and potassium is $C_2(OK)_2$. Above 170°C the product is mostly $C_6(OK)_6$. The latter is what is usually called potassium carbonyl.

Hexaphenol is an important intermediate in the manufacture of leuconic acid, tetrahydroxyquinone, and other organic chemicals. (5) It is oxidized by the air, does not melt, but turns dark at 200°C.

Hexaacetoxybenzene can be formed directly from the carbonyl as described above, or can also be formed from hexaphenol, by reaction with acetic anhydride.

The reaction for this formation is as follows:

$$C_6(OH)_6 + 6(CH_3CO)_2O = C_6(OOCCH_3)_6 + 6\ CH_3COOH$$

There is no mention of sodium carbonyl in the literature. Since sodium is chemically very similar to potassium, and the reaction between potassium and carbon monoxide is thought to be vapor phase, it is probable that any reaction between sodium and carbon monoxide would be vapor phase also.

The vapor pressures of sodium and potassium, as functions of temperature can be determined from the equations of the Internation Critical Tables. (7)

Potassium $$\mathrm{Log}_{10}P = \frac{-4430}{T} + 7.183$$

Sodium $$\mathrm{Log}_{10}P = \frac{-5400}{T} + 7.553$$

P is pressure in mm. of mercury and T is temperature in degrees Kelvin.

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