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A STUDY OF THE CONDENSATION OF
CHLOROFORM AND ACETOPHENONE
A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry

by Alfred Lewis

Approved by R.W. Finkelt

June, 1948
INTRODUCTION

Condensation products of ketones and aldehydes have been known and studied for some time with both aromatic and aliphatic compounds.

J. W. Howard and co-workers (1-4) have studied the condensation reaction of chloroform with several compounds. Condensation products have been reported with benzaldehyde, furfural, p-chlorobenzaldehyde, o-chlorobenzaldehyde, m-chlorobenzaldehyde and p-tolualdehyde.

Other evidence has shown that chloroform forms condensation products with aldehydes and ketones. Cryoscopic measurements show condensation products as evidenced by deviation from predicted freezing point lowerings. (5) Ultraviolet adsorption data also indicates formation of condensation products of this nature. (6)

Ekeley and Klemme showed that methyl ethyl ketone and acetone form condensation products with chloroform. (7) Their work showed that methyl ethyl ketone forms an addition product in an analogous fashion as Jocic postulated with benzaldehyde and chloroform. (8)
Jocicz offered the idea of the formation of an intermediate complex compound during the reaction. For example, the reaction of benzaldehyde and chloroform in the presence of a solid base, KOH, is shown below:

\[
\text{\begin{chemicalreaction}
\text{H} & \text{C} = \text{O} \quad + \quad \text{KOH} \quad \rightarrow \quad \text{H} \quad \text{C} = \text{O} \quad \text{OK}
\end{chemicalreaction}}
\]

\[
\text{\begin{chemicalreaction}
\text{H} \quad \text{C} = \text{O} \quad \text{OK} \\
\text{H} \quad \text{O} \\
\end{chemicalreaction}} \quad + \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{KOH} \quad + \quad \text{Cl} \quad \text{H} \quad \text{O} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

The above postulated mechanism of the reaction has been accepted by workers in this field.

Many compounds, both aldehydes and ketones, fail to form condensation products with chloroform. Attempts by Howard and co-workers (1) to form condensation products with formaldehyde, acetaldehyde, propionic, butyric, iso-valeric, or salicylic aldehydes have failed. Ekeley and Klemme failed in their attempt to form a condensation product with acetophenone. (7)
The condensation reaction is generally carried out in the presence of a solid base. The experimental procedure employed by Howard and coworkers (1) is as follows:

"Equimolar quantities of reacting materials are placed in an erlenmeyer flask. A finely powdered dry solid base (KOH was principally used) was added with stirring. The reactions proved highly exothermic and cooling was necessary. The solid base was added in small portions over a period of 1-3 hours. Ethyl ether was then added, and the mixture filtered. The chloroform and ether were distilled over a steam bath and the remaining aldehyde or ketone removed by distillation under reduced pressure."

Ekeley and Klemme (7) report the characteristics of the condensation product formed with ethyl methyl ketone as "a yellow liquid, relatively stable in the absence of light, possessing a pungent odor and producing a numbing sensation when placed on the tongue."

Since it has been shown that benzaldehyde and chloroform successfully form a condensation product, it was felt that despite previous failure (7) a condensation product of chloroform and
acetophenone could be produced. No reference was made in the literature of the time of reaction or conditions which accompanied the unsuccessful attempts with acetophenone.

Possibly steric hindrance effects may be the cause for failure of the acetophenone and chloroform to react. Therefore, in my attempt to carry out the reaction, the experimental conditions were adjusted to keep the reacting compounds together for long periods of time under varying conditions of temperature, pressure, and solid base catalysts.

The reaction desired is shown below:

\[
\text{Cl-C-Cl} + \text{Acetophenone} \rightarrow \text{Product}
\]
EXPERIMENTAL PROCEDURE

Purification of reacting materials

**Chloroform**

The chloroform was twice distilled and the fraction boiling at 61-62°C was collected. The boiling point of chloroform is 61.2°C. The refractive index was measured with an Abbe Refractometer. The value 1.4491 compared favorably with the actual value 1.4464.

**Acetophenone**

The acetophenone was twice distilled and the fraction boiling at 202-203°C was collected. The boiling point of acetophenone is 202.3°C. The refractive index was measured (1.5340) and it compared favorably with the actual value of 1.5342.

The molecular weight of chloroform is 119.39 and that of acetophenone 120.14. Since they are almost equal, equal weights of chloroform and acetophenone were used in the reactions. 20 cc. of chloroform (specific gravity 1.49) and 30 cc. of acetophenone (specific gravity 1.03) were the volumes of reacting materials used.
2 grams of powdered KOH (pellets ground with mortar and pestle) were placed in a 500 cc. round bottomed flask with 10 cc. of benzene. The benzene was distilled off and the acetophenone and chloroform were added simultaneously to the dry KOH. The mixture turned reddish brown and some gas was evolved.

This was attributed to the solution of the KOH in the acetophenone and the reaction of the KOH with the chloroform forming potassium formate. (7) This typical reaction was observed whenever the acetophenone and chloroform were added to the various solid bases used. (KOH, Ca(OH)_2, Ba(OH)_2)

This mixture was connected to a reflux condenser equipped with a CaCl_2 drying tube and refluxed for 1 1/2 hours. 20 cc. of ethyl ether were added, the mixture filtered, and the ether distilled. The remaining mixture was distilled and came over at 202-203° C. It consisted chiefly of acetophenone and some chloroform.

This procedure was repeated using Ba(OH)_2 and Ca(OH)_2. The results indicated that the chloroform reacted with the solid base but failed to
form a condensation product.

Using the different solid bases, the reaction mixtures were refluxed for longer periods of time ranging from 75 to 100 hours. Again no indication of a condensation product was evidenced.

Aqueous mixtures of 2 grams of solid base in 20 cc. of water were added to the acetophenone and chloroform mixture and the mixtures refluxed 6-8 hours. The liquid layers were separated and revealed no condensation product.

Refractive indices of mixtures of chloroform and acetophenone were measured with an Abbe Refractometer. These were plotted on a graph from which it is seen the percentage of either component can be readily obtained.

**REFRACTIVE INDICES OF MIXTURES OF CHLOROFORM AND ACETOPHENONE**

<table>
<thead>
<tr>
<th>Percentage volume acetophenone vs. R.</th>
<th>R.I.</th>
<th>Percentage</th>
<th>R.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.5340</td>
<td>40</td>
<td>1.4890</td>
</tr>
<tr>
<td>90</td>
<td>1.5270</td>
<td>30</td>
<td>1.4802</td>
</tr>
<tr>
<td>80</td>
<td>1.5250</td>
<td>20</td>
<td>1.4712</td>
</tr>
<tr>
<td>70</td>
<td>1.5145</td>
<td>10</td>
<td>1.4621</td>
</tr>
<tr>
<td>60</td>
<td>1.5062</td>
<td>0</td>
<td>1.4491</td>
</tr>
<tr>
<td>50</td>
<td>1.5000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The solid base was dissolved in the 30 grams of acetophenone, the excess filtered off, and this solution added to 30 grams of chloroform with subsequent refluxing. This was accomplished using each of the three solid bases. Again results failed to show any evidence of an addition product.

Having failed to accomplish any suitable reaction, I attempted to utilize pressure methods. A 'Coca-Cola' bottle, tightly stoppered with a rubber stopper which was wired in place, was the reaction vessel used.

30 grams of each reactant were placed in the bottle and the top securely sealed. The bottle was placed in an oil bath and heated to approximately 200° C. One unsuccessful attempt resulted in blowing the stopper and starting an oil fire. However, another attempt failed to show any product as indicated from refractive index data. The condition of the bottle, cracked internally, indicated severe pressure had existed in the reaction vessel.

This was repeated using the various solid bases. The results again failed to show any evidence of a condensation product.
SUMMARY

As a result of the work performed, it is believed that under ordinary conditions chloroform and acetophenone fail to react to form an addition product.

One of the major set-backs appears to be the reactivity of the solid bases with the chloroform. Perhaps some 'condensation agent' which fails to react with either the chloroform or the acetophenone will produce the desired effect.

The steric hindrance effect does not seem to be sufficient to stop the reaction in view of the success achieved with benzaldehyde, a molecule comparable in size to acetophenone. An unfavorable equilibrium might be a contributing factor.
BIBLIOGRAPHY

(1) Journal American Chemical Society 47-455-1925 J.W.Howard

(2) " " " " 57-2317-1935 "

(3) " " " " 57-376-1935 "

(4) " " " " 60-229-1938 "

(5) Journal Chemical Society p.707 1928 Magdin,Peel & Briscoe


(7) Journal American Chemical Society 46-1252-1924 Ekeley & Klemme


(9) "Organic Chemistry" p. 254 Whitmore