| Title       | The Study on the Reaction of Acetylene under High Pressure.  

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Kyoto University
1) Adhesive mixture.
   Resin 10 gr.
   Calcium hydroxide (solid) 3-5 gr.

2) Specific pressure applied.
   About 18 kg/cm² (adhesive strength 150-180 kg/cm², wet adhesive strength about 50 kg/cm²).

3) Pressing time and temperature.
   5-10 min. at 110-140°C.

4) Amount of Spread.
   Resin 1 gr. per 50-55 cm² area.

5) Working life of this mixture.
   About 5 days at 5°C
   About 15 hours at room temperature.

6) The excellent adhesive strength is obtained by addition of 1% wood powder (80-120 mesh) besides calcium hydroxide and 30% sodium hydroxide solution.


64. The Study on the Reaction of Acetylene under High Pressure. (II)
Preparation of Unsaturated Higher Aldehydes.

Junji Furukawa and Nobuho Saito.

(Oda Laboratory)

The reaction of acetylene with water under high pressure and at high temperature in the presence of weak basic salt, which is the usual catalyst for such reaction under high temperature, gave unsaturated higher aldehydes and small quantity of aldehyde resin. Zinc acetate, a weak basic salt was used as catalyst. In this case, the yield of aldehyde resin was influenced by temperature, time and presence of solvent. Benzene was found suitable as the solvent, as it is water insoluble and a good solvent for the products. Pressure and temperature have an advantageous effect on the velocity of acetylene-absorption.

Experiment: In a 1/4-autoclave are put 255 g-water, 45 g-zinc acetate, 1 g-acetic acid and 0.5 g-hydroquinon.

Then the air in the autoclave was replaced by N₂, and acetylene was pressed in to 22.5 atom. The autoclave was shaked at 158°C for 4 hours. After cooling, upper benzene layer was separated from reaction mixture, dried, and distilled in CO₂ atmosphere. The following table shows the fractions of the product.
Each fraction 1–5 reacted with Schiff's reagent, semicarbazid, and Na-bisulfite. Physical constants of purified fraction 1 were compared with those of reaction product of crotonaldehyde with acetaldehyde \(^1\),

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Pressure mmHg</th>
<th>B. P.</th>
<th>Yield</th>
<th>(n_D^m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>55–63°C</td>
<td>8.5 g</td>
<td>1.5225</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>63–72°C</td>
<td>1.5 (\star)</td>
<td>1.5154</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>80–92°C</td>
<td>2 (\star)</td>
<td>1.5510</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>90–120°C</td>
<td>4 (\star)</td>
<td>1.4780</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>120–125°C</td>
<td>2 (\star)</td>
<td>1.5225</td>
</tr>
<tr>
<td>Residue (resin)</td>
<td></td>
<td></td>
<td>3.5 (\star)</td>
<td></td>
</tr>
</tbody>
</table>

The products of this reaction are likely to be the same products made by R. Kuhn's method or those isomers, and we are expecting to decide their exact constitutions by means of reduction of the products.

Literature.

1) R. Kuhn and Coworkers: Ber. 69, 98, (1936)


*Katsuhiko Ichikawa, Tadashi Mizoguchi and Haruo Shingu.*

(Kodama Laboratory)

\(\phi\)-Hydroxyphenyl mercuric halides (\(\phi\)-HgX) decompose quantitatively with HX:

\[
\text{HOC}_6\text{H}_4\text{HgX} + 3 \text{HX} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{HgX}_4.
\]

The reaction was studied kinetically by determining the conc. of \(\phi\)-HgX iodometrically. (I) The rate of the decomposition of \(\phi\)-HgCl with HCl could be expressed completely by

\[
-\frac{d(a-x)}{dt} = k_1(a-x)(b-3x),
\]

where Cl\(^-\) conc. had no effect upon the reaction rate. \(k_1\): 0.0491 at 50°C, 0.1183 at 60°C, 0.269 at 70°C, 0.591 at 80°C respectively. (II) The reaction rate of \(\phi\)-HgI with HI was shown to be expressed by

\[
-\frac{d(a-x)}{dt} = Kk_3(a-x)(b-3x)(b'-3x),
\]

which holds as well when KI is added. \(Kk_3\): 17.2 at 0°C, 30.5 at 10°C respectively. (III) The decomposition of \(\phi\)-HgBr with HBr at 80°C and at 90°C was the same as in (I) with small conc. of Br\(^-\), the second-order rate constant being 1.86 and 3.58 respectively. With large conc. of Br\(^-\), however, the rate equation could be best expressed by

\[
-\frac{d(a-x)}{dt} = k_2(a-x)(b-3x) + k_1'(a-x),
\]

where \(k_2\) is the second-order constant as found above and \(k_1'\) is a variable and increases with the conc. of Br\(^-\).