

- 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.
- 1) R. Nodzu, R. Goto and Y. Kozai; "Wood Research" Bulletin of The Wood Research Institute, Kyoto University. 4 (1950) 50.

64. The Study on the Reaction of Acetylene under High Pressure. (II)

Preparation of Unsaturated Higher Aldehydes.

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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 1l-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 shaken 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.

Fraction	Pressure mmHg	B. P.	Yield	n_D^{20}
1	12	55-63°C	8.5 g	1.5225
2	10	63-72°	1.5°	1.5154
3	10	80-92°	2°	1.5510
4	6	90-120°	4°	1.4780
5	6	120-125°	2°	1.5225
Residue (resin)			3.5°	

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 acetaldehyde¹⁾,

	B. P.	n_D^{20}	D	M
Fraction 1	74-76°C/30mm	1.5330	0.9055	96
Hexadienal	76°C/30mm	1.5372	0.9087	95

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)

65. Kinetics of the Decomposition of o-Hydroxyphenyl Mercuric Halides with Hydrohalogenic Acids.

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O-Hydroxyphenol mercuric halides (ϕ -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 ϕ -HgX iodometrically. (I) The rate of the decomposition of ϕ -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 ϕ -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 ϕ -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^-