Electrolytic Reduction of Benzaldehyde at a Mercury Cathode—Preparation of Dibenzyl Mercury

By Toshio ARAI and Tsuneto OGURI

(Received February 12, 1960)

Many studies have already been carried out on the electrolytic reduction of aldehydes, with the result that usually their reduction tends to form resinous materials. There is no doubt that the formation depends upon electrolytic conditions employed. In the case of lead or mercury cathode which has a high hydrogen overvoltage, resinous materials are easily formed.

It has been reported that the electrolytic reduction of ketones in sulfuric acid solution at a mercury cathode produces organomercury compounds[1-3]. The present investigation was undertaken to prepare organomercury compounds from aldehydes which have the carbonyl radical as ketones. Consequently, a way was found to produce dibenzyl-mercury from benzaldehyde. However, other aldehydes such as vanillin, piperonal, anisaldehyde, furfural and salicyl aldehyde were not reduced to their mercury compounds under the same conditions, and resinous materials were easily formed.

The experiment was carried out according to the procedures described previously[3]. Benzaldehyde was shaken with 5% sodium carbonate solution several times, dried and distilled prior to use. The electrolysis was carried out under following conditions: cathode, mercury 15.2 cm^2; cathodic solution, 50% sulfuric acid in which 15 g. of benzaldehyde was suspended; electric current, 3 A. (current density 19.7 A./dm^2); time of electrolysis, 7.5 hr. A 50% sulfuric acid served as anodic solution and cylindrical lead was employed as anode. The anolyte was separated from the catholyte by a porous pot.

As the electrolysis proceeded, a pale yellow material floated on the surface. After the electrolysis, the product was collected on a funnel and sucked as much as possible to give solid residue. It was recrystallized from ethanol several times to give needle crystals, m. p. 110°C (the reported value, 111°C)[4], yield being about 2.4 g., 8.5% of theoretical amount.

Found: Hg, 52.56. Calcd. for $C_{14}H_{14}Hg$: Hg, 52.40%.

When the compound in the product was heated with ethanol solution of mercuric chloride, mercuric bromide and mercuric acetate, benzylmercuric chloride (m. p. 103°C. plates from ethanol-xylene), benzylmercuric bromide (m. p. 118°C, plates from ethanol) and benzylmercuric acetate (m. p. 126°C, needles from ethanol) were obtained respectively.

Found for benzylmercuric chloride: Hg, 61.69. Calcd. for C_7H_7HgCl: Hg, 61.31%.

In this reduction under the conditions described above, hydrobenzoin was also obtained, but it was separated completely by recrystallizing several times with ethanol.

The temperature of reduction was found to have influence on the yield of dibenzyl mercury. Temperatures below 25°C gave the favorable dibenzyl mercury yields, but at 50°C only oily material and hydrobenzoin were obtained.

In an attempt to compare the influence of concentration of sulfuric acid on the yield of dibenzyl mercury, experiments were made at several concentrations. It was found that 50% sulfuric acid was the most efficient catholyte and a lower acidity resulted in the decrease of the yield.

It was also found that the current density had no effect between 20 and 40 A./dm^2.

The authors express their sincere thanks to Professor Buhei Sakurai for his kind guidance and encouragement throughout the present experiment.

Department of Chemistry
Faculty of Liberal Arts and Science
Shinshu University
Matsumoto

---

1) J. Tafel, *Ber.*, 39, 3626 (1906).

2) C. J. Haggerty, *Trans. Am. Electrochem. Soc.*, 56, 421 (1929).

3) T. Arai, This Bulletin, 32, 184 (1959).

4) P. Wolff, *Ber.*, 46, 64 (1913).