Electrolysis of Benzile.

Thesis for M.S. 1899.

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THE ELECTROLYSIS OF BENZIL.

Laurent, Zinin, and Klingen were among the first to study benzil. Laurent prepared it by passing chlorine into benzoin.

$$C_6H_5CHOHCOC_6H_5 + 2Cl = C_6H_5COCOC_6H_5 + 2HCl.$$

Zinin prepared it by heating gently one part of benzoin with two parts of concentrated nitric acid; the reactoin is complete when no morenitrous fumes are given off. Klingen heats benzoyl chloride with sodium amalgam.

Benzil crystallizes by spontaneous evaporation of its ethereal, alcoholic or chloroform solution, in long yellow hexagonal prisms. It is odorless, tasteless, insoluble in water, soluble in alcohol, ether, chloroform and warm sulphuric acid. It melts between 92° and 95° C. It is not altered by boiling with consentrated nitric acid. It sublimes unchanged. When boiled with alcoholic potash it turns blue and forms benzilic acid. In the reduction of benzaldehyde by means of the electric current, Kauffmann obtained hydrobenzoin. The process was carried on in the presence of acid potassium sulphite, which formed with the aldehyde

$C_6H_5C(H)(OH)(KSO_3)$ By reducing this through the use of the porous cylinder, the KSO_3 was removed leaving the radical $C_6H_5C(OH)H$ which combined with a similar one forming hydrobenzoin, as we well as the isomeric form $C_6H_5C(OH)(H)-C(H)(OH)C_6H_5$ and finally by oxidizing these substances with nitric acid, normal benzil was was obtained. Later benzoin was reduced by the current forming benzoinpinacone.

C_6H_5CHOH
C_6H_5COH
C_6H_5COH
C_6H_5CHOH

Benzil was also reduced and formed an isomeric substance which was tetraphenylerythrit.

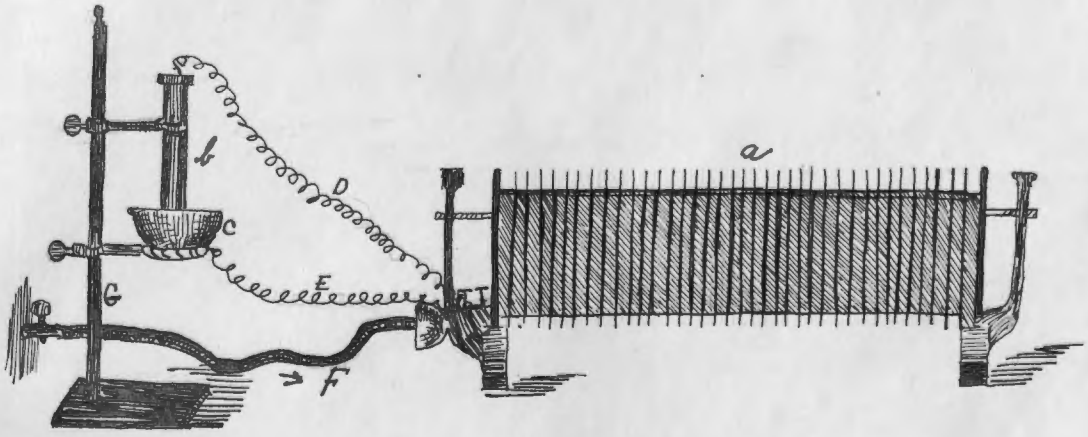
(1) Zeitschrift F. Electrochemie II, 365

(2) Zeitschrift F. Electrochemie IV, 461.

EXPERIMENTAL.

Benzil seemed to be the most inviting on account of its easy mode of formation and the number of different substances obtained by varying the strength of the current and whether it was positive or negative. The apparatus used in the following experiments consisted of a large size Gülcher thermopile with platinum dishes and porous cylinders.

The cylinders giving the best results were the porous form as Pasteur filter. The Pukal filter was tried but was not satisfactory on account of its density. The following is a sketch of the apparatus:



A= Thermopile
B= Porous cylinder
C= Platinum dish
D= Electrode
E= "
F= Gas
G= Ring stand.

REDUCTION OF BENZIL IN AN ALCOHOLIC ETHER SOLUTION.

Benzil was dissolved in alcohol- ether solution, transferred to a platinum dish and electrolized for eighteen hours. The dish was the negative pole. A fine white p precipitate was obtained which when purified and dried, melted at 138° C. This substance was electrolized, the current being reversed, a yellow precipitate was obtained, which melted at 95° C. This substance upon careful examination was found to be a mixture of benzoin and hydrobenzoin.

REDUCTION IN ALCOHOL- AMMONIA.

Benzilwas dissolved in alcohol-ether and strong ammonium hydrate added, electrolized in a platinum dish which was made the negative pole. A white crystalline precipitate was obtained, which when dried and purified, by recrystallizing out of alcohol, melted at 144-145° C. The properties of this substance have not been studied.

OXIDATION OF BENZIL IN ALCOHOL-ETHER SOLUTION.

Benzil was dissolved in alcohol, strong ammonia added, then electrolized for twenty hours, the dish being positive. A fine white precipitate was obtained which

when treated with chloroform was found to be two different substances, one having needle-like crystals, soluble in cold chloroform, melting point 148-150° C, the other hexagonal shaped prisms or columns, insoluble in the cold chloroform, melting point 173° C.

Analysis of this substance gave the following results:

I. 0.188 grams dried substance gave 0.5196 grams carbon dioxide and 0.089 grams water.

II 0.198 grams dried substance gave 0.542 grams carbon dioxide. and 0.0956 grams water.

III 0.2144 grams dried substance gave 7.3 c.c. gas. Barometric pressure 732. Temperature 25° C.

IV 0.1958 grams dried substance gave 7.1 c.c. gas. Barometric pressure 730. Temperature 25° C.

Calculated for	Found.			
$C_{42}H_{40}N_2O_6 + H_2O$.	I.	II.	III.	IV.
C = 75.22	75.38	74.87		
H = 6.25	5.21	5.36	3.64	3.87
N = 4.19				

The substance is insoluble in ethyl, methyl, or amyl alcohol, benzol, toluene, petroleum ether, ethyl ether, acetone, water, ammonia and dilute acids. Burns with a sooty flame. Concentrated nitric and hydrochloric acids dissolve it forming benzil. Concentrated sulphuric breaks it down forming a dark gray powder, which melts above 315° C. It was first thought that it might belong to one of the following compounds:

Imabenzil $C_{35}H_{28}N_2O_3$. Benzilimide. $C_{21}H_{17}NO_2$.

Benzilam $C_{21}H_{19}NO$ Lophine $C_{21}H_{16}N_2$.

These compounds were first prepared and studied by Laurent. Imabenzil forms small orthorhombic crystals, melting point 194° C. It is slightly soluble in hot alcohol, more soluble in hot methyl alcohol. When it is heated with water benzilam is formed, benzaldehyde, benzoic acid and ammonia. By treating benzilam with alcoholic potash it is converted into benzilimide. Benzil and alcoholic ammonia heated to 130° C for several hours forms Lophine, (Henius). Reference: Watt's Chemical Dictionary.

It can easily be seen from the above reactions that the

ammonia compound prepared by electrolysis does not correspond to any of these prepared by Laurent. The percentage, composition and melting points also do not agree.

ACTION OF BROMINE ON THIS AMMONIA COMPOUND.

This ammonia compound was treated with liquid bromine, stirred vigorously and allowed to stand fifteen minutes; a dirty yellow substance was obtained, which melted at 150°-155°. This mass was treated with ether and alcohol, apparently most of it dissolved. Water was now added and a light yellow precipitate was obtained, which was dried and melted at 90°-92°. The bromine acted probably as an oxidizing agent and formed benzil.

OXIDATION IN ETHER, CHLOROFORM OR DILUTE AMMONIA.

When benzil was electrolized in ether solution and a few cubic centimeters of ammonia added, no results were obtained. The benzil had all crystallized out. The same happened when chloroform was used or dilute ammonia. When chloroform and alcohol solution of benzil was electrolized and a few cubic centimeters of ammonia added; a yellow, oily, resinous mass was obtained.

ACTION OF CUPRENT ON ALCOHOL AND AMMONIA.

About fifty cubic centimeters of alcohol and ten of ammonium hydrate were transferred to a platinum dish which was the positive pole and electrolized for twelve hours Apparently no results were obtained. The solution was evaporated down on a water bath nearly to dryness; allowed to crystallize and long white needles were obtained, which when dried and purified melted at 75-81° C. This substance was probably ammonia aldehyde. The current oxidizing the alcohol to the aldehyde and then the ammonia acting on the aldehyde to form ammonia aldehyde.

OXIDATION OF BENZIL IN ALCOHOLIC POTASH SOLUTION.

Benzil was dissolved in alcohol- ether solution about five grams of stick potash was added and a current passed through for twelve hours; the dish being the positive pole. Obtained a dark red liquid which was put on a water ba bath evaporated nearly to dryness, allowed to crystallize out, dried and obtained a yellow powder which did not melt at 310° C. It had a strong odor of benzaldehyde. The powder was treated with ether to dissolve the out any unconverted

benzil, filtered and washed until the filtrate was colorless. The filtrate was evaporated nearly to dryness, allowed to crystallize , obtained a yellow powder melting at above 310°. This powder was now dissolved in hot water, dilute hydrochloric acid added until it gave an acid reaction, obtained a heavy, flocculent, yellowish colored precipitate, filtered off and recrystallized the precipitate out of hot water. Melting point of the purified substance was 115-116° C. This substance is readily soluble in hot water, alcohol and ether. When heated in a glass tube it sublimes unchanged. It burns with a sooty flame. Analysis of the dried substance gave the following results:

I. 0.2312 grams of dried substance gave 0.594 grams of carbon dioxide and 0.1058 grams of water.

II. 0.2146 grams of dried substance gave 0.5524 grams of carbon dioxide and 0.994 grams of water.

III. 0.210 grams of dried substance gave 0.544 grams of carbon dioxide and 0.1256 grams of water.

Calculated for	Found		
$(C_6H_5)_2(CHOH)_4$	I.	II.	III.
C = 70.07	70.07	70.139	70.03
H = 6.50	5.082,	5.13	6.[illegible]