however that in the catalytic oil cracking processes, the catalyst combines with certain products in the reaction so that the unsaturated portion of the oil is held back from the distillate.

Summary.

1. Experiments upon the formation of a series of compounds between anhydrous aluminium chloride and some of the simpler unsaturated organic compounds have been described.

2. A number of such compounds are described and their analyses given.

3. The hypothesis that similar products are formed during the cracking of oils has been suggested.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE HENRY PHIPPS INSTITUTE OF THE UNIVERSITY OF PENNSYLVANIA.]

ON THE ELECTROLYTIC DIAZOTATION OF AN ALIPHATIC COMPOUND.

BY ROBERT B. KRAUSS.

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Introduction.

In the course of the preparation of a large number of new azo dyes and our study of their relation to the chemotherapy of tuberculosis during recent years, it became desirable to synthesize compounds containing aliphatic side chains linked to benzol and naphthalene rings through the N-N group. Since the literature of the diazo reaction held but little prospect of a method of general application along strictly chemical lines, our attention was turned to the development of the electrolytic method suggested for aromatic derivatives by Löb.[1]

Historical.

The diazo reaction was discovered by Peter Griess[2] in 1862 and carefully studied by him. On adding a concentrated potash solution to diazo benzene chloride, he obtained potassium diazotate. In 1894 Schraube and Schmidt[3] observed that diazo benzene chloride and strong caustic heated together to 130–140° gave a salt isomeric with Griess' salt, an isodiazotate. It did not have the property of forming azo colors directly with an alkaline phenol, but regained this property on making it acid first and then adding it to an alkaline phenol. In the next thirty years countless attempts were made to diazotize aliphatic amino compounds and isolate or couple them. It was found that the amino group was replaced by a hydroxy group and that the intermediate diazo compound was not stable.

[1] *Z. Electrochem.*, 10, 237 (1904).

[2] *Ann.*, 121, 257 (1862); 137, 39 (1866).

[3] *Ber.*, 27, 514 (1894).

About 1888 Curtius[1] on replacing the reactive hydrogen atom of the carboxyl group of glycocoll by the ethyl or methyl group, was able to obtain, by treatment with nitrous acid, diazo acetic esters. It was also found that compounds having NH_2 in the alpha position to CO or CN formed similar diazo derivatives, which were however less stable than the esters.

Pechman[2] later found that acylated nitrosamines when treated with sodium hydroxide decomposed into diazomethane, also that alkylamine in the form of its urethane, would react with nitrous acid to form a nitrosamine which could in turn be hydrolyzed by alkali to diazomethane.

Hantzsch and Lehman[3] investigated this reaction and concluded that methyl azotate, the hydrate of the diazo compound, was formed but broke down into its anhydride.

In short, none of these methods produce aliphatic diazonium salts analogous to the reactive aromatic diazonium salts but instead form non-reactive diazo anhydrides and their derivatives.

Löb discovered that azo dyestuffs could be made by electrolysis. To obtain them he dissolved molecular quantities of the amine, sodium nitrite and the second component in water and passed a current through the solution. The reagents were placed in an anode compartment which was separated from the cathode by a porous cell. The usefulness of this method is restricted by the fact that only phenols can be used as second components. Löb insisted that the second component must be present in the solution so that the diazo compound as fast as formed should be coupled and removed from the zone of reaction. The remarkable feature of this method is that no artificial cooling is necessary. In the strictly chemical diazotations, temperatures between 0° and 10° must be maintained.

Method.—A consideration of the various points involved in the problem led us to lay down the following working conditions as those which might probably be successful:

To fix the diazo salt at the instant of its formation, before it passed into its anhydride.

To maintain a low temperature to permit of its formation.

To diazotize electrically avoiding the use of acid.

On account of accessibility, the substance chosen for our experiments was glutamic acid.

Preparation of Glutamic Acid.—Of the amino acids glutamic is the most readily isolated in quantity since its hydrochloride is insoluble in concentrated hydrochloric acid. When prepared by the hydrolysis of

[1] *J. prakt. Chem.*, **38**, 407 (1888).

[2] *Ber.*, **28**, 855 (1895).

[3] *Ibid.*, **35**, 901 (1902).

protein the only difficulty lies in the initial crystallization of the hydrochloride. The viscosity of the solution due to the presence of other amino acids in quantity seems to greatly retard the formation of crystals, which at best are very small and hard to filter. The following procedure gives satisfactory results with yields of about 10%:

The most economical raw material is casein. 1500 g. of commercial casein are added to 4.5 liters of concentrated hydrochloric acid contained in an 8-liter round-bottom flask. The protein is then hydrolyzed by boiling under a reflux condenser. It is convenient to boil for 24 hours, but less time is probably sufficient. The biuret test may be applied to determine complete hydrolysis.

When cool the solution is filtered to remove fat and humin and concentrated to 2.4 liters. After standing in an ice box for at least 24 hours, the mass should be filtered on a Büchner funnel. After washing with a little absolute alcohol the glutamic acid hydrochloride is dissolved in just sufficient hot water and filtered. The solution is saturated with hydrochloric acid and set in the ice box to crystallize. The hydrochloride is again filtered, washed and dissolved.

The solution, somewhat diluted, is boiled with animal charcoal and after concentrating, saturated with hydrochloric acid. Filter, wash with absolute alcohol and dry. The glutamic acid hydrochloride should be pure white.

Glutamic acid is prepared by neutralizing with caustic soda. 183 g. glutamic acid hydrochloride are dissolved in 350 cc. hot water. 40 g. caustic or proportionally more, if it is not anhydrous, are dissolved in 50 cc. water. The alkali is then added very slowly to the hot glutamic solution, all the time stirring vigorously. The precipitate should be crystalline and settle rapidly. It is filtered off when cold and washed with a little water and then with alcohol. Dry at 110°. The glutamic acid should be white and free from chloride.

Apparatus.—A small stoneware crock was used as the cathode chamber. This was placed inside a larger one with an insulation of cotton waste between. A 300 cc. porous cup placed inside the cathode chamber formed the anode chamber.

Methyl alcohol chilled by passing through a copper coil submerged in an ice and salt mixture is pumped by an electrically driven gear pump through a glass coil in the anode in series with a copper coil in the cathode chamber, and then returned to the cooler.

The anode consists of a circular platinum gauze electrode 3 cm. in diameter rotated at about 200 r. p. m. by motor.

The cathode is the copper cooling coil in the cathode chamber.

During the experiment the temperature has been kept between 0° and —2° for the most part. It has occasionally fallen to —4°.

Current.—The direct current was obtained from a motor generator set and then suitably regulated by resistance on a special switchboard making it possible to obtain any current from 0.01 to 10 amperes at convenient voltage steps. During these experiments the current was maintained at 3.5 amperes and 7 volts.

Electrolytes.—The anode electrolyte used was glutamic acid in an excess of caustic soda solution with the addition of sodium nitrite, the quantities of each being varied as shown below;

	Molecular.	2.	3.	4.	5.
Glutamic acid	45	45	45	30	30
Sodium nitrite	21	25	25	30	30 (In grams)
Sodium hydroxide	36	50	80	34	75

The cathode electrolyte was 30% caustic soda solution.

Result of Electrolysis.—When the current is passed through any of the foregoing mixtures under the stated conditions the solution gradually acquires an orange-yellow color. After numerous trials it was found that a run of about four hours with electrolyte mixture No. 4 gave a maximum of orange color in the anode chamber. Electrolyzing for an indefinite additional period caused no change in color.

Separation.—The anode solution is then removed from the apparatus, filtered and treated in a 3-liter flask with about 1 liter absolute ethyl alcohol, until a yellow oil begins to separate at the bottom of the flask. After allowing to stand about a half hour the alcoholic solution is decanted from the oil and placed in a vessel to be recovered. The oil is now transferred to a 500 cc. beaker and washed twice with 200 cc. alcohol, decanting each time. This produces a thick syrup which is treated with 200 cc. 98% methyl alcohol. This changes it to a pasty mass to which is added about 5 cc. water. If the electrolysis is incomplete, flocculent glutamic acid will separate when the methyl alcohol treatment is begun and can be decanted with the alcohol. After again treating with methyl alcohol decanting and repeating the solution and precipitation four times, the substance is free from sodium nitrite and is a solid. It is sucked dry on a small Büchner funnel and warmed in an electric oven.

The dry substance obtained in this way is a cream-colored amorphous solid and contains impurities consisting chiefly of sodium carbonate. On solution in water a yellow liquid is obtained. This substance when sufficiently washed should not give a test for nitrite, using acetic acid for acidulation and testing with starch-iodide mixture.

Reactions.—The substance itself contains nitrogen and gives the pyrrolpine splinter test on heating.

By the Shotten-Baumann reaction with chlorobenzoyl chloride a crystalline solid is obtained, melting at 191°. This compound contains nitrogen. The corresponding glutamic acid derivative melts at 140°.

With β-naphthalene sulfochloride, a crystalline solid melting at 185–186° was obtained. This also contained nitrogen. The corresponding glutamic acid derivative melts at 163°.

When the substance dissolved in water and mixed with aniline is acidulated with hydrochloric acid below 0°, a yellow color is formed becoming deep red with excess of acid. Similarly with α-naphthylamine a deep red color is formed.

A water solution of the substance separately mixed with a solution of the following, made just acid below 0° and then alkaline, produces colors as follows: 1,8-Amido naphthol 3,6-disulfonic (H) acid, a deep blue; 1,8-dioxynaphthaline 3,6-disulfonic acid (Chromotrope), a violet; sodium β-naphtholate a yellow color. These colors do not have the intense staining qualities of the purely aromatic azo dyes.

Discussion.

It seems probable in the light of these reactions that the isoazotate of glutamic acid is formed by the above-described process. The analytical data to establish this point conclusively is not available at this time because of the extreme difficulty attending the purification of the substance for analytical purposes.

A method is now being developed to avoid decomposition and remove the inorganic matter which unfortunately has about the same solubilities as the substance in question.

It is our purpose to present in the near future the necessary analytical data to establish the constitution of this new substance as well as additional data for derivatives and new condensations. Work is under way at this time to apply this method to other suitable aliphatic amino compounds.

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[CONTRIBUTION FROM THE HENRY PHIPPS INSTITUTE OF THE UNIVERSITY OF PENNSYLVANIA.]

THE PREPARATION OF HALOGEN DERIVATIVES OF CATECHOL, HONO-CATECHOL AND PYROGALLOL METHYL ETHERS AND SULFONIC ACIDS.

BY ROBERT B. KRAUSS AND EDWARD CREDE.

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Introduction.—The attention of this laboratory has been directed during recent years towards the synthesis of tetrazo and disazo dyes for the purpose of chemotherapeutic experimentation on tuberculosis.

Using benzidine and its derivatives as the base, numbers of dyes have been prepared by diazotizing them and coupling to amino and phenolic