[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, INDIANA UNIVERSITY.]

CATALYTIC PREPARATION OF THE AMIDOPHENOLS AND THE PHENYLENEDIAMINES.

BY O. W. BROWN AND L. L. CARRICK.

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The writers for some time have been preparing *o*-amidophenol from *o*-nitrophenol by the well-known electrolytic process of Löb and Elbs.[1] These methods give a yield of only about sixty per cent. of the theory and the *o*-amidophenol obtained is impure and dark in color. The writers have tried to purify it by recrystallization, but have only been able to obtain a pure, colorless product by sublimation of the impure material. These difficulties led the writers to attempt the preparation of *o*- and *p*-amidophenol by the general method of catalytic hydrogenation of volatile compounds, first used by Paul Sabatier and J. B. Senderens.[2] When it was found that the catalytic method of preparing *o*-amidophenol gave practically quantitative yields of a pure, colorless product, the writers also tried this method of preparing the phenylenediamines.

M. G. Mignonac[3] has obtained the amidophenols from the corresponding nitrophenols by the Sabatier method. He states that the nitrophenols are converted into the corresponding amidophenols by passing their vapors, mixed with hydrogen, over divided nickel at a temperature of 160° to 190°. He states that the reduction of a nitrophenol to an amidophenol is accompanied by the formation of ammonia, phenol and traces of aniline. Mignonac used nickel only for a catalyst. The writers have experimented with copper as a catalyst, and have also made a further study of the preparation of the amidophenols when nickel is the catalytic agent. The method herein described is an improvement on the work of Mignonac.

Procedure.—Our general plan of procedure was to bubble hydrogen through the molten nitro compound, to convey the mixed hydrogen and nitro-compound vapors over the hot catalyst, and to collect the resulting solid and liquid products in a suitable receiver. The solid nitro compound was placed in a distilling flask completely surrounded by an air bath, and the rate of vaporization was easily governed by the temperature of the flask and the velocity of the current of hydrogen. The side neck of the distilling flask connected directly with the furnace in which was placed a train of 60 centimeters of catalyst. The furnace consisted of a one-half inch iron pipe projecting two inches beyond the ends of a two-inch iron pipe. The two-inch iron pipe was wrapped with one layer of

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[1] Löb, *Z. Elektrochem.*, **2**, 533 (1896); Elbs, *J. prakt. Chem.*, **43**, 39 (1891).

[2] *Ann. chim. phys.*, [8] **4**, 319–490 (1905).

[3] *Bull. soc. chim.*, [4] **7**, 270 (1910).

asbestos paper, on which No. 18 nichrome wire was wound, and the whole was surrounded with four thicknesses of asbestos paper. Rings, cut from one-fourth inch thick asbestos board, that fitted snuggly into the ends of the two-inch iron pipe, were slipped over the one-half inch iron pipe to make an air-tight jacket surrounding the reaction tube. The asbestos rings were fastened in place by sodium silicate cement.

The temperature of the furnace could be well controlled by adjusting a sliding resistance connected in series with the nichrome wire and a 110-volt direct current circuit. The reaction products from the furnace passed into a glass receiver over which cold hydrant water was kept running. The solid in every instance collected just outside the mouth of the furnace in a pure condition, while the liquid products were found in the lower end of the receiver.

Uniform conditions were very carefully maintained throughout any run. The rate of adding the hydrogen was regulated by a wash bottle. The furnace was brought to the desired temperature and kept at this temperature for one hour before making a run to insure the temperature of the air in the air bath and the reaction tube being the same. The temperature was determined by a thermometer within the air jacket. If there was any excessive local heating, due either to uneven winding or a difference in resistance of the nichrome wire, it was dissipated by the two-inch iron pipe, and the air bath. This insured equal heating in all parts of the reaction tube.

Catalyst.—The catalyst used was prepared by boiling pumice stone, crushed to pass a quarter-inch sieve, several hours in a saturated solution of the nitrate of the metal, pouring off the excess of nitrate solution, calcining at a dark red heat in an electric furnace, placing the pumice stone impregnated with oxide in the reaction tube, heating to 325°, and reducing the oxide to metal in a current of hydrogen. After reduction was complete the tube was securely stoppered until desired for use. The hydrogen employed in this reduction and in subsequent hydrogenation was prepared by electrolysis and was found to be sufficiently pure. In preparing a catalyst of pure metal free from inert material the nitrate of the metal was ignited to the oxide at a dark red heat in an electric furnace and then reduced to metal in a current of hydrogen as described above. An iron tube was used to contain the catalyst as it does not catalytically affect the nitro grouping to any appreciable extent below 400°.

Preparation of *o*-Amidophenol.—The vapors of *o*-nitrophenol with an excess of hydrogen, passed over recently reduced copper on pumice stone maintained between 210° and 315°, yield beautiful, colorless, crystalline plates of *o*-amidophenol which without purification melts at 170°. As no side products are produced, the reduction of the *o*-nitrophenol presumably takes place according to the reaction represented by the following equation:

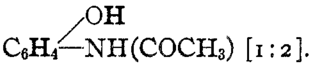
$$OH.C_6H_4.NO_2 + 3H_2 = OH.\ C_6H_4.NH_2 + 2H_2O$$

The yield of *o*-amidophenol appears to be quantitative. It may be kept in an atmosphere of hydrogen without darkening, but on exposure to air it takes on the redish tinge found in the commercial product.

If the temperature of the catalyst is raised above 315°, the product is charred and the yield diminished. Below 210° the transformation is not complete. The writers consider that a temperature around 265° is most suitable for the reaction. No appreciable deterioration of the catalyst was noticed after it had been used many times.

On passing the vapors of *o*-nitrophenol with an excess of hydrogen over recently reduced nickel, capable of transforming benzene into cyclohexane, heated between 170–180°, crystalline plates of *o*-amidophenol (m. p. 170°), long needles with the prongs perpendicular to the main axis of the crystal (m. p. 170°), and a little phenol and ammonia were formed. At this temperature the product condenses on the catalyst and soon reduces its activity, but not sufficiently to stop the decomposition of the nitrophenol into phenol and ammonia. As the temperature of the catalyst is raised the formation of the crystalline plates of *o*-amidophenol decreases, while the formation of the needle-like crystals, and of phenol and ammonia increases, and at about 200°, we have no further formation of crystalline plates of *o*-amidophenol, but a maximum yield of the crystalline needles. There is a gradual decrease in the yield of the crystalline needles and an increase in that of phenol and ammonia as the temperature is further elevated.

The acetyl derivative of the crystalline needles was prepared and gave a melting point of 201°, corresponding to that of the acetyl derivative of *o*-amidophenol.



$$C_6H_4\begin{array}{l}\diagup OH\\ -NH(COCH_3)\end{array}[1:2].$$

From a consideration of this and the fact that the crystalline needles melt at the same temperature as *o*-amidophenol, it appears certain that the needles are *o*-amidophenol and that *o*-amidophenol can exist in either of two crystalline forms, depending upon the catalyst used and the temperature at which the compound is produced.

When reduced nickel on pumice was substituted for reduced nickel alone, no crystalline plates of *o*-amidophenol were formed. The reduced nickel on pumice would not transform benzene into cyclohexane. For some reason the pumice stone reduces the activity of the nickel.

When any form of nickel catalyst is used a small amount of phenol and ammonia is always formed along with the *o*-amidophenol. And this product darkens much faster than that formed over a copper catalyst. Moreover, as no ammonia, phenol or other side products are produced with copper this metal is much better for use in the production of *o*-amidophenol than is nickel.

Preparation of *p*-Amidophenol.—If the vapors of *p*-nitrophenol with an excess of hydrogen are passed over reduced copper or pumice stone maintained between 210–310°, one obtains without any complications, pure white needles of *p*-amidophenol, melting at 183°. If a temperature of 180° to 190° is employed the transformation is not complete. The formation of *p*-amidophenol is slower than that of the *o*-amidophenol, as the *p*-nitrophenol is not so volatile as the *o*-nitrophenol.

Preparation of *o*-Phenylenediamine.—On slowly passing the vapors of *o*-nitroaniline with an excess of hydrogen over reduced copper on pumice stone, heated between 210–320°, there is a total transformation of the *o*-nitroaniline into *o*-phenylenediamine. This method of preparing *o*-phenylenediamine is slow because the *o*-nitroaniline is only slightly volatile below its decomposition point.

Preparation of *p*-Phenylenediamine.—When *p*-nitroaniline is heated to 195°, and the vapor at this temperature, with an excess of hydrogen, is passed over reduced copper on pumice stone, heated between 200–300°, there is a total transformation of the *p*-nitroaniline into *p*-phenylenediamine (m. p. 140°). The *p*-nitroaniline is only very slightly volatile and on this account the preparation of *p*-phenylene diamine by this method is too slow for practical purposes.

Preparation of *m*-Phenylenediamine.—The vapors of *m*-nitroaniline with an excess of hydrogen passed over reduced copper on pumice stone heated between 255–310°, yield only *m*-phenylenediamine. This substance may be prepared quantitatively and much faster by passing the vapors of the more volatile *m*-dinitrobenzene with an excess of hydrogen over reduced copper on pumice stone, maintained between 270–310°. The transformation into *m*-phenylenediamine is, however, not complete at any lower temperature.

Summary.

1. The method described affords an easy commercial means of preparing *o*-amidophenol from *o*-nitrophenol.

2. Copper is superior to nickel as a catalyst in preparing *o*-amidophenol, because with copper the *o*-nitrophenol is reduced quantitatively to *o*-amidophenol; while with a nickel catalyst there is always some formation of side products.

3. It is shown that nickel deposited on pumice stone is less active than pure nickel prepared in the same manner, but without the pumice stone.

4. When only small quantities of *p*-amidophenol or *m*-phenylenediamine

are desired the method given here is applicable as the product is obtained pure.

5. The preparation of the phenylenediamines from nitroanilines by this method is extremely slow, due to the slight volatility of the nitroanilines.

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A STUDY OF THE ACTION OF 10% THYMOL-CHLOROFORM PRESERVATIVE ON THE CHLORINE CONTENT OF URINE.[1]

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The effect of thymol-chloroform as a urinary preservative on the chlorine content, both in acid and alkaline urines, was studied over longer and shorter periods of time.

The advantages of chloroform thymol over the alcoholic thymol as a urinary preservative lies in its convenience, the small quantities necessary and the avoidance in the case of toluol of an insoluble layer on the surface of the urine. Thymol-chloroform is being more widely used.

What effect the presence of chloroform would have on the chlorine content was not known. It was desirable to keep the urines liquid near freezing temperature rather than frozen and hence it was deemed advisable to ascertain what this effect would be.

TABLE I.—THE EFFECT OF CHLOROFORM AS A PRESERVATIVE ON THE CHLORINE CONTENT OF SWINE URINE PER 100 CC.

Sample.	Det. No.	Control. Gms. Cl.	Preserved. Gms. Cl.	Acidity. Cc. 0.1 *N* NaOH.	Added preservative. Cc.
1	1	..	0.3369	117	0.4
	2	0.3375	0.3372	...	0.8
2	3	0.3170	0.3165	112	0.4
	4	..	0.3159	...	0.8
3	5	0.2672	0.2685	101.1	0.5
4	6	0.2326	0.2319	92.1	0.5
5	7	0.2515	0.2502	82.2	0.5
6	8	0.2437	0.2415	84.8	1.0
7	9	0.2584	0.2591	72.1	1.0
8	10	0.2672	0.2700	70.1	1.0
9	11	0.1655	0.1773	85.0	1.0
10	12	0.1617	0.1689	17.5	1.0
11	13	0.1090	0.1129	22.1	1.0
12	14	0.2343	0.2395	88.8	1.0
13	15	0.3155	0.3232	24.7	1.0
14	16	0.4072	0.4108	30.9	1.0

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[1] An abstract of this work was presented at the Cleveland meeting of the American Chemical Society, September 10, 1918.