

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF PITTSBURGH]

**THE CATALYTIC REDUCTION OF ALPHA-NITRONAPHTHALENE
TO ALPHA-NAPHTHYLAMINE¹**

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RECEIVED NOVEMBER 23, 1925

PUBLISHED MARCH 5, 1926

In this research a study was undertaken of the liquid phase catalytic reduction of α -nitronaphthalene to α -naphthylamine. The use of hydrogen under moderate pressures (50 and 100 lbs. or $3\frac{1}{3}$ and $6\frac{2}{3}$ atmospheres), a variety of catalysts, and vigorous agitation by stirring seemed to offer possibilities for the development of a method generally applicable to the reduction of organic compounds. The variable factors studied were temperature, pressure, catalysts, time of reaction and type of solvent.

α -Nitronaphthalene has been catalytically reduced to α -naphthylamine by Sabatier and Senderens.² They conducted vaporized α -nitronaphthalene with hydrogen over nickel at 300° , the corresponding amine being formed. At 330° they found that ammonia was evolved and naphthalene and tetrahydronaphthalene resulted. Similarly, copper was used to reduce α -nitronaphthalene at 300 – 350° to the amine with satisfactory results.

Nitro compounds have been reduced by various other methods under a variety of conditions but a literature search reveals only the above-reported case of the catalytic reduction of α -nitronaphthalene.

Experimental Part

Apparatus.—A small laboratory autoclave equipped with a stirrer capable of being operated at 1000 r.p.m. was used. The cylinder of the autoclave was jacketed by an oil-bath and was fitted inside with a glass tube 63.5 mm. in diameter. This tube was used to hold the reaction mixture and was so arranged that the stirrer dipped into the liquid to the proper depth. The stirrer was of nickel so that none of the steel of the autoclave came into contact with the catalyst or with the reaction mixture. The autoclave was provided with a thermometer well, inlet and outlet valves and a pressure gage. The pressure was easily regulated at 50 and 100 lbs. ($3\frac{1}{3}$ and $6\frac{2}{3}$ atmospheres).

In operating the autoclave, it was first brought up to the desired temperature by means of the oil-bath jacket. Then the glass tube containing the reaction mixture was inserted and the lid placed in position. The

¹ Presented before the organic section of the American Chemical Society at its Baltimore Meeting, April 6–11, 1925.

This paper is a condensed report of a thesis presented by Arthur N. Parrett to the Faculty of the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for degree of Doctor of Philosophy, 1925.

² Sabatier and Senderens, *Compt. rend.*, **135**, 225 (1902).

lid was tightened by eight radial bolts. The apparatus was, in every experiment, flushed out with hydrogen five times by alternately raising the pressure to the maximum used, and then allowing the gas to escape. The solution was then stirred at a constant stated rate for the desired length of time. Then the apparatus was opened, the glass tube removed, and the catalyst filtered off as quickly as possible to avoid catalytic oxidation.

Preparation of Catalysts and Reagents.—The palladium black used in this investigation was prepared by an adaptation of the well-known method of reducing palladous chloride with formaldehyde in the presence of sodium hydroxide. Methods for the preparation of palladium black have been described by Breteau,³ Loew⁴ and Willstätter.⁵

The platinum oxide, $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$, used as catalyst was prepared by the method of Adams and Shriner.⁶ The method of the same authors⁷ was used for the preparation of palladium oxide catalyst, PdO . Although the directions of these authors were carried out as exactly as possible, successive preparations of platinum oxide were of slightly different color. They seemed, however, to be uniformly active as catalysts.

The nickel catalyst used was prepared by calcining c. p. nickel nitrate at a dull red heat. The oxide thus formed was reduced in a combustion furnace, a stream of hydrogen passing over the nickel continuously. The maximum temperature during the reduction was 325° . Fresh catalyst was prepared for each experiment and was added to the reaction mixture just before the autoclave was closed to avoid prolonged contact with air.

The α -nitronaphthalene used in the experiments was prepared by the nitration of naphthalene with subsequent steam distillation to remove the excess of naphthalene. It was further purified by crystallization four times from 95% ethyl alcohol. It was pale yellow and melted at 58.0 – 58.5° .

The solvents used were purified by distillation. No attempt was made to dry them.

Method of Analysis.—The percentage of α -nitronaphthalene reduced to α -naphthylamine in each experiment was determined by diazotization with a standardized solution of sodium nitrite. In case the solvent was ethyl or isopropyl alcohol, the solvent was first evaporated on a steam-bath. The α -naphthylamine was dissolved in dil. hydrochloric acid and the solution made up to a definite volume in a volumetric flask. Then aliquot portions were titrated by the following method.

By means of a pipet a 50- or 100cc. portion of the solution prepared as described above was removed and diluted to 150 cc., and 20 cc. of concd. hydrochloric acid was added. The solution was then cooled to 0 – 5° and titrated with $0.1020 N$ sodium nitrite

³ Breteau, "Div. Meth. D'hydr. app. au Phenant," Paris, 1911, p. 25.

⁴ Loew, *Ber.*, **54**, 121 (1921).

⁵ Willstätter, *Ber.*, **54**, 123 (1921).

⁶ Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).

⁷ Adams and Shriner, *ibid.*, **46**, 1683 (1924).

solution which was added in 5cc. portions at first until the titration was within 5 cc. of the end-point, the solution being stirred continuously. Then smaller portions were added, and the presence of an excess of nitrous acid tested for by means of starch iodide solution on a porcelain drop plate. In this way a point was reached at which the addition of two drops of sodium nitrite solution produced an immediate blue color on the test plate. When tested two minutes later, however, no coloration resulted. At the end-point chosen, a test made on a plate five minutes after the time of the addition of two drops of sodium nitrite solution showed a decided blue coloration immediately. At least two portions were titrated in each case.

Experiments Using Palladium Black as Catalyst.—A series of preliminary experiments using glycol as a solvent were made. These were for the purpose of determining the effect of using the two stated pressures and the efficiency of glycol as a solvent. Stirring was conducted at 1000 r.p.m., 0.200 g. of palladium black was used as catalyst and 100 cc. of glycol as solvent.

TABLE I
EXPERIMENTS USING PALLADIUM BLACK AS A CATALYST
Temperature, 70°

Expt.	Press., atm.	Wt. of α -nitro-naphthalene, g.	Time in hours	Reduction to amine, %
1	3 $\frac{1}{3}$	5.00	7.5	89.40
2	3 $\frac{1}{3}$	5.00	3	84.62
3	6 $\frac{2}{3}$	5.00	3	98.44
4	6 $\frac{2}{3}$	10.00	3	96.25
5	6 $\frac{2}{3}$	15.00	3	92.16

The experiments of Table I indicate a decided advantage in using the higher hydrogen pressure over the lower. Further experiments were therefore made (Table II) using 6 $\frac{2}{3}$ atmospheres pressure and more concentrated solutions. Other solvents were tried, using multiples of the concentrations of the solutions used in the previous experiments. To effect better stirring 125 cc. of solvent was used. Thus 15.00 g. of α -

TABLE II
EXPERIMENTS AT 6 $\frac{2}{3}$ ATMOSPHERES PRESSURE WITH MORE CONCENTRATED SOLUTIONS
18.75 g. of α -nitronaphthalene, taken in each experiment except No. 8, in which 37.50 g. was used.

Expt.	Time, hours	Solvent	Temp., °C.	Reduction to amine, %
6	3	Glycol	70	95.34
7	1.5	Glycol	70	66.87
8	3	Glycol	70	91.90
9	1.5	Glycol	50	61.23
10	1.5	Glycol	70	66.87
11	1.5	Glycol	85	85.94
12	1.5	Glycol	100-105	93.49
13	3	Glycerol	70	64.12
14	1.5	<i>iso</i> Propyl alcohol	70	96.22
15	1.5	Water	70	76.79
16	3	Water	70	94.70

nitronaphthalene in 100 cc. of solvent corresponded to 18.75 g. in 125 cc. of solvent. Stirring was at 1000 r.p.m. and 0.500 g. of palladium black was used as catalyst in each experiment.

Expts. 7 and 10 in Table II are the same experiment, shown twice for the purpose of comparison. Expts. 6 and 7 indicate the time effect, Expts. 6 and 8 the concentration effect, and Expts. 9, 10, 11 and 12 the effect of increasing the temperature, all with glycol as solvent. Expts. 13, 14, 15 and 16 indicate the relative merits of glycerol, *isopropyl* alcohol, and water as solvents at 70°. One interesting possibility is that each solvent has a temperature of maximum efficiency with a particular catalyst. Insufficient data were obtained for such a comparison.

Experiments Using Platinum and Palladium Oxides as Catalysts.—The experiments of Table III were made using platinum and palladium oxides as catalysts, during stirring at the rate of 1000 r.p.m., and under a pressure of $6\frac{2}{3}$ atmospheres. Equimolecular portions of platinum and palladium metal were used in experiments 17, 18, 19 and 20. In these experiments the temperature variation was greater than in previous experiments, where the temperature variation was not over 5° unless so tabulated. The heat of reaction which caused the temperature variation was especially manifest during the first part of the reaction.

TABLE III
PLATINUM AND PALLADIUM OXIDES AS CATALYSTS

Expt.	α -Nitro-naphthalene, g.	Catalyst	Wt., g.	Time, hours	Solvent	Temp., °C.	Reduction to amine, %
17	18.75	PtO ₂ ·2H ₂ O	0.43	1.5	125 cc. glycol	80-100	90.42
18	18.75	PtO ₂ ·2H ₂ O	.43	1.5	125 cc. ethyl alcohol	60-90	95.34
19	18.75	PdO	.215	1.5	125 cc. ethyl alcohol	60-70	94.51
20	18.75	PdO	.215	1.5	125 cc. ethyl alcohol	70-90	94.90
21	100.0	PdO	1.00	3	110 cc. ethyl alcohol	70-100	94.24
22	200.0	PdO	2.00	3	No solvent	100-110	93.90

Expts. 20, 21 and 22 indicate that the concentration of α -nitronaphthalene may be increased up to the point of using pure molten α -nitronaphthalene without any solvent with only very slight diminution in the percentage reduced to amine, provided the same proportion of catalyst is used. Expts. 17 and 18 show ethyl alcohol to be more efficient than glycol. The amount of solvent used in Expt. 21 was such that the total volume of the reaction mixture was approximately 125 cc., since all of the α -nitronaphthalene did not dissolve but remained molten as a separate phase.

Experiments Using Nickel as a Catalyst.—The experiments listed in Table IV indicate that the particular nickel catalyst used was not as active as the platinum and palladium catalysts. Doubtless better percentage yields could be obtained with other nickel catalysts, such as those dispersed on an inert material or a combination copper and nickel catalyst. All of these possibilities could not be followed out in this investigation.

TABLE IV
NICKEL AS CATALYST

Expt.	α -Nitro-naphthalene, g.	Nickel, g.	Time, hours	Solvent 125 cc.	Temp., °C.	Reduction to amine, %
23	18.75	1.00	1.5	Glycerol	150	1.92
24	9.375	1.00	1.5	Glycerol	240	22.78
25	9.375	1.00	1.5	Kerosene	240	38.94
26	18.75	1.00	3	Liquid petrolatum	240	9.51
27	18.75	2.00	1.5	Glycol	180	35.46
28	18.75	2.00	3	Glycol	180	70.56
29	18.75	2.00	3	Ethyl alcohol	70	2.95
30	175.00	7.00	3	No solvent	250	14.32

Expts. 23 and 24 indicate the much greater activity of the nickel catalyst at 240° as compared to 150°.

Summary

1. Preliminary experiments were conducted showing that α -nitronaphthalene can be catalytically reduced to α -naphthylamine with palladium black as catalyst and glycol as solvent. Larger yields were obtained with 6²/₃ atmospheres pressure of hydrogen than with 3¹/₃ atmospheres.

2. α -Nitronaphthalene was reduced in glycol with palladium black as catalyst at temperatures ranging from 50° to 100°. The percentage reduced to α -naphthylamine increased with the temperature.

3. Glycerol, glycol, water and *isopropyl* alcohol were used as solvents with palladium black as catalyst. The efficiency of these media increased in the order given.

4. Palladium oxide and platinum oxide were used as catalysts and produced high percentage yields of α -naphthylamine in one and a half hours. These catalysts appear to be efficient.

5. Molten α -nitronaphthalene was reduced with palladium oxide as catalyst with a yield of 93.90% (Expt. 22), and with nickel with a yield of 14.32% (Expt. 30).

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