ester isolated from the ammoniacal solution as in the preparation above. This acid ester was refluxed in 2 *N* aqueous sodium hydroxide for an hour, then the solution steam distilled. The *l*-ethylethynylcarbinol was salted out of the distillate with potassium carbonate, dried and distilled.

Reductions.—A modification of the apparatus described before[19] was used in which the reduction vessel had a capacity of 125 cc.

A solution of 3.8 cc. of *l*-ethylethynylcarbinol in 10 cc. of pure dry ethyl acetate was shaken with 0.08 g. of platinum oxide catalyst and hydrogen for twenty hours, during which time 1660 cc. (S. T. P.) of hydrogen was absorbed. Since the solution still showed a slight optical activity, indicating incomplete reduction, it was shaken for sixty hours more with hydrogen. The rotation of the solution had then dropped to zero and the product was removed from the solvent by fractional distillation through a 30-cm. column packed with a helix of nichrome wire having about three turns per cm. The same column was used in purifying all the other samples of carbinols.

The reduction of 4.7 cc. of the active carbinol in 15 cc. of ethyl acetate with 0.1 g. of catalyst and practically 100% deuterium was carried out in exactly the same way and used 1900 cc. (S. T. P.) of gas. The solution was slightly active after the first twenty hours and was shaken sixty hours more. The solution had then no detectable rotation. The product was isolated from the solvent by distillation as above.

One-tenth mole of *d,l*-ethylethynylcarbinol in ethyl acetate solution was reduced with hydrogen by the same procedure using 0.2 g. of catalyst. The product was isolated in the same way and its 3,5-dinitrobenzoate prepared by the procedure described for that of ethylethynylcarbinol. Glistening white needles were obtained, m. p. 99.0–99.5°.[20]

Anal. Calcd. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found (Dumas): N, 10.03.

A pure sample of ethyl-d_4-ethylcarbinol was prepared by reduction of 0.1 mole of *d,l*-ethylethynylcarbinol with practically 100% deuterium and isolation in the same way. The 3,5-dinitrobenzoate prepared as above melted at 98.5–99.0°. A mixture of this derivative and that of diethylcarbinol showed no melting point depression.

Anal. Calcd. for $C_{12}H_{10}D_4O_6N_2$: N, 9.79. Found (Dumas): N, 9.45.

Summary

Ethylethynylcarbinol was partly resolved to give a *levo* form with high optical activity.

Reduction of this carbinol with hydrogen and with deuterium gave products polarimetrically indistinguishable in that neither had a detectable rotation in the pure state.

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[19] McLean and Adams, THIS JOURNAL, 56, 504 (1936).

[20] M. p. 97° given by Boese, Jones and Major, *ibid.*, 53, 3530 (1931).

URBANA, ILLINOIS RECEIVED JUNE 14, 1937

[CONTRIBUTION NO. 34 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Catalytic Reduction of Some Azo Compounds and its Application to the Identification of Azo Dyestuffs

BY WILLET F. WHITMORE AND ANTHONY REVUKAS

Introduction

The earliest catalytic reduction of an azo compound is that reported thirty-one years ago by Sabatier and Senderens.[1] They hydrogenated azobenzene in the vapor phase at 290° with a nickel catalyst and obtained chiefly aniline and small amounts of cyclohexylamine, dicyclohexylamine, and ammonia. Skita[2] got hydrazobenzene in five minutes and aniline in four and one-half hours with colloidal palladium under two atmospheres pressure. Brown and Henke[3] are patentees of a method for the reduction of azo and azoxy compounds with a nickel catalyst and hydrogen at 16.7 and at 33.3 atmospheres pressure and 100°, in which they claim good yields of the corresponding hydrazo compounds. More recently Winans and Adkins[4] have hydrogenated *p*-dimethylaminoazobenzene-*p*-sodium sulfonate at 100° and 100 atmospheres pressure, to *p*-sodium sulfanilate and *p*-dimethylaminoaniline within one hour over a nickel catalyst adsorbed on infusorial earth. With azobenzene, an ammonium carbonate type nickel catalyst on a kieselguhr support at 200° and 100–150 atmospheres pressure, they obtained 22% cyclohexylamine, 21% aniline, and 48% dicyclohexylamine in eight and one-half hours. At 90° a 95% yield of aniline was obtained within thirty minutes.[5] Andrews and Lowy[6] have investigated the catalytic reduction of azobenzene and *p*-aminoazobenzene in contact with platinum and with Raney nickel at 3 atmospheres pressure. They were interested primarily in the conditions

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[1] Sabatier and Senderens, *Bull. soc. chim.*, 35, 259 (1906).

[2] Skita, *Ber.*, 45, 3312 (1912).

[3] Brown and Henke, U. S. Patent 1,589,936, June 22, 1926.

[4] Winans and Adkins, THIS JOURNAL, 54, 311 (1932).

[5] *Ibid.*, 55, 2055 (1933).

[6] *Ibid.*, 56, 1411 (1934).

necessary for a maximum yield of hydrazobenzene, and concluded that platinum is the better catalyst.

The large number of azo compounds which constitute the industrially important azo dyestuffs warrant special attention, since there is an urgent need of a simple, yet precise, procedure for their analysis and estimation. The analysis of these types is best effected by reduction and recognition of the basic forms produced. This reduction is normally carried out with stannous chloride, sodium hyposulfite, etc., which not only contaminate but make the isolation of the scission products more difficult.

This investigation is the first of a series which, it is hoped, will demonstrate the practicality of the Raney nickel catalyst for the hydrogenolysis of azo and substituted azo compounds at room temperature and from 1 to 4 atmospheres absolute pressure.

Materials.—C. P. azobenzene, purified by several recrystallizations from ligroin. *p*-Dimethylaminoazobenzene-*p*-sodium sulfonate (methyl orange), an indicator grade, recrystallized several times from water. *p*-Dimethylaminoazobenzene-*o*-carboxylic acid (methyl red), prepared and purified according to directions in "Organic Syntheses."[7]

The following is a list of other water soluble sulfonated azo compounds studied: sodium-*p*-sulfobenzeneazo-α-naphthol (Orange I); sodium-*p*-sulfobenzeneazo-β-naphthol-6-sodium sulfonate (Sunset Yellow); sodium-*p*-sulfonaphthaleneazo-β-naphthol-3,6-disodium disulfonate (Amaranth); 2,4,5-trimethylbenzeneazo-β-naphthol-3,6-disodium disulfonate (Ponceau 3R), 1-sodium-*p*-sulfobenzene-3-sodium carboxy-5-pyrazolone-4-azo-benzene-*p*-sodium sulfonate (Tartrazine).

Azo dye	Moisture, %	NaCl, %	Insol., %	Color by difference, %	Color by $TiCl_3$ titration, %
Orange I	2.86	2.47	0.20	94.47	91.67
Sunset Yellow	2.93	1.85	.09	95.13	87.33
Amaranth	6.26	1.99	.09	91.66	91.04
Ponceau 3R	5.44	4.77	.06	89.73	91.93
Tartrazine	4.42	3.30	.04	92.24	90.65

The Raney nickel catalyst was prepared according to the method of Covert and Adkins.[8]

Method

That quantity of azo compound which was *completely* soluble in 125 ml. of the solvent was shaken with 3–5 g. of the Raney nickel catalyst per 0.01 mole of the substance. The hydrogenolysis was carried out either at 45 lb. (3 atm.) gage pressure and room temperature using the Burgess–Parr apparatus,[9] or at one atmosphere absolute pressure, in which case the hydrogen was supplied from a 200-ml. buret and the Burgess–Parr agitation equipment was used. After one hour, or when no further absorption of hydrogen occurred, the contents of the reaction vessel were filtered rapidly to remove the spent catalyst. Usually one of the reaction products was extracted with ethyl ether, and the other precipitated out by introducing hydrogen chloride gas into the filtrate.

The volume of hydrogen absorbed at atmospheric pressure corresponds to the percentage of hydrogenolysis and is a quantitative indication of the purity of the dye or azo compound. Although the cleavage is quantitative at atmospheric pressure, it does not appear to be so at four atmospheres absolute pressure. This anomaly may be explained by the fact that the quantity of azo compound to be reduced is limited both by the volume of the reaction vessel, and by the solubility of the substance in that particular volume of solvent that is employed. With the size of sample used in this investigation, the total drop in pressure rarely exceeded 4 lb. (207 mm.), which corresponded to 4 scale divisions on the gage. The pressure could not be read with a precision greater than 0.2 lb. (10.2 mm.). This introduced an error of 5%.

Discussion

The catalytic reduction of relatively simple azo compounds at from 1–4 atmospheres absolute pressure and room temperature may be accomplished with Raney nickel catalyst. The basic reaction consists in the scission of the molecule at the azo grouping with the formation of two amines. For example the cleavage may be symbolized thus

$$R—N{=}N—Rx + 2H_2 \longrightarrow RNH_2 + RxNH_2$$
$$x = NH_2, OH, CH_3, SO_3Na$$

The azo compound to be investigated preferably should be entirely soluble in the solvent selected. The best results are obtained in a neutral or slightly alkaline solution. The presence of mineral acid hinders the absorption of hydrogen and may even prevent it entirely. Delépine and Horeau[10] have studied this behavior with Raney nickel catalyst and have shown that minute additions of alkali materially accelerate the reaction.

Water is an excellent medium for the hydrogenolysis of the sulfonated azo compounds. The cleavage products, however, are exceptionally sensitive to atmospheric oxidation, so that isolation and purification in satisfactory yield is complicated.

Catalytic reduction with the Raney nickel is of practical value in the analysis of the water-soluble sulfonated azo dyes as well as the other azo compounds mentioned in this paper. Both the

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(7) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York City, 1932, p. 366.

(8) Covert and Adkins, This Journal, 54, 4116 (1932).

(9) Gilman, "Organic Syntheses," Coll. Vol. I. John Wiley and Sons, Inc., New York City, 1st ed., 1932, p. 53.

(10) Delépine and Horeau, *Compt. rend.*, **202**, 995 (1936).

EXPERIMENTAL RESULTS

All reductions were made at room temperature (22–27°), and the solvent used was distilled water in each case, except azobenzene which required absolute ethanol. Methyl Red was made water soluble by adding the necessary amount of sodium hydroxide previous to hydrogenation.

H_2 acceptor	Moles	Catalyst, g.	*P*, absolute atm.	Time, min.	% hydrogenolysis	Products	Yield G.	Yield %
Azobenzene	0.05	15	4	60	100	Aniline[a]	8.9	96
Methyl orange	.02	10	4	20	94	*p*-Aminodimethylaniline[b]	2.0	74
						Sulfanilic acid[c]	3.2	92
Methyl orange	.03	15	1	65	99.7	*p*-Aminodimethylaniline	3.0	73
						Sulfanilic acid	4.1	80
Methyl red	.03	15	1	68	99.8	*p*-Aminodimethylaniline	3.0	73
						Anthranilic acid[d]	3.7	90
Orange I	.03	15	4	60	89.7	1-Hydroxy-2-aminonaphthol[e]	2.0	42
						Sulfanilic acid	3.7	71
Orange I	.03	15	1	49	91.5	1-Hydroxy-2-aminonaphthol hydrochloride	4.0	75
						Sulfanilic acid	4.5	80
Sunset yellow	.03	15	4	35	83.3	1-Amino-2-naphthol-6-sulfonic acid[f]	1.9	26
						Sulfanilic acid	2.7	52
Sunset yellow	.03	15	1	62	88.0	1-Amino-2-naphthol-6-sulfonic acid	3.1	43
						Sulfanilic acid	3.7	71
Amaranth	.02	10	4	62	90.7	Na salt of 1-amino-2-naphthol-3,6-disulfonic acid[g]	4.2	58
						Naphthionic acid[h]	3.0	70
Amaranth	.02	10	1	47	91.0	Na salt of 1-amino-2-naphthol-3,6-disulfonic acid	5.0	69
						Naphthionic acid	3.6	80
Ponceau 3R	.02	10	4	61	87.5	1,2,4,5-Cumidine[i]	2.5	93
						1-Amino-2-naphthol-3,6-disulfonic acid[j]	5.0	78
Ponceau 3R	.02	10	1	50	91.9	1,2,4,5-Cumidine	2.5	93
						1-Amino-2-naphthol-3,6-disulfonic acid	4.3	67
Tartrazine	.02	10	4	60	87.5	4-Amino-1-(4)-sulfophenyl-5-pyrazolone-3-carboxylic acid[k]	1.2	20
						Sulfanilic acid	1.5	43
Tartrazine	.02	10	1	93	92.1	4-Amino-1-(4)-sulfophenyl-5-pyrazolone-3-carboxylic acid	2.7	45
						Sulfanilic acid	3.0	87

[a] After filtering to remove catalyst, the solvent was distilled off under reduced pressure on the water-bath; derivative, tribromoaniline, m. p. 118°. [b] The filtrate was extracted with ether. The extract was dried over anhydrous sodium sulfate and finally subjected to a distillation at reduced pressure to remove the ether; derivative, *p*-acetylaminodimethylaniline, m. p. 130°. [c] The aqueous ether-extracted solution was surrounded with an ice–salt mixture and hydrogen chloride gas introduced until precipitation occurred. Oxidation of the precipitate with manganese dioxide and dilute sulfuric acid gave yellow benzoquinone, m. p. 115°. [d] The isolation procedure was the same as for (*b*). The hydrochloric acid insoluble product melted at 144° and with benzaldehyde formed benzalamino-*o*-benzoic acid, m. p. 128°. [e] The reduced solution was extracted with ether. After drying over anhydrous sodium sulfate, the ether extract was surrounded with ice–salt mixture and hydrogen chloride gas introduced until a precipitate formed. Three grams of this product, together with 3 g. of anhydrous sodium acetate and 18 ml. of acetic anhydride, were refluxed for two hours at 60–70°. After cooling the reaction mixture was poured into water and the solid filtered off. Upon recrystallizing from methanol the compound melted at 162°, which corresponded to the diacetyl derivative of 1-hydroxy-2-amino-naphthol (Koch, B.S. Thesis, 1936, Polytechnic Institute of Brooklyn). [f] The filtered reduced solution was treated with 0.5 ml. of concd. hydrochloric acid and cooled slightly. The precipitate which formed was purified by dissolving it in the least possible quantity of water containing 0.7 g. of anhydrous sodium carbonate and a little sodium sulfite, filtered, surrounded with an ice–salt mixture, and hydrogen chloride gas introduced. Small colorless needle-like crystals were obtained. *Anal.* Calcd. for $C_{10}H_9O_4NS$: C, 50.13; H, 3.79; S, 13.40. Found: C, 50.02; H, 3.82; S, 13.31. [g] The sodium salt will precipitate out if the reduced solution is permitted to stand for several hours. The product, which is insoluble in alcohol and ether, may be purified by quickly dissolving 0.5 g. in 15 ml. of water containing 1 ml. of concd. hydrochloric acid and filtering to remove undissolved particles. One ml. more of concd. hydrochloric acid is added to the filtrate and the solution is then immersed in an alcohol–dry ice bath until small white silky needles deposit. The compound is 1-amino-2-naphthol-3,6-disulfonic acid. *Anal.* Calcd. for $C_{10}H_9O_7NS_2$: C, 37.59; H, 2.84; S, 20.08. Found: C, 37.44; H, 2.79; S, 20.00. [h] Naphthionic acid was isolated by means of hydrogen chloride gas and identified by boiling with 75% H_2SO_4 to form naphthylamine, m.p. 50°. [i] The reduced filtered solution was extracted with ether. The ether extract was dried over anhyd. sodium sulfate and finally heated on the water-bath to remove the ether. The residue was acetylated and after recrystallization from water melted at 154°. The melting point of the acetyl derivative of 1,2,4,5-cumidine is recorded in the literature as 161°. [j] The disulfonic acid can be isolated from the reduced ether-extracted solution by surrounding with ice–salt mixture and introducing hydrogen chloride gas. [k] Since the reduced solution is very sensitive to air and becomes purple, it must be filtered as rapidly as possible to remove the spent catalyst. When 1 ml. of concd. hydrochloric acid is added to the filtrate which is cooled slightly, a faintly lavender colored product is obtained. The substance may be purified by dissolving in 25 ml. of water containing 1 g. of anhyd. sodium carbonate, immersing in an ice–salt mixture, and introducing hydrogen chloride gas until precipitation occurs. *Anal.* Calcd. for $C_{10}H_9O_6N_3S$: C, 40.11; H, 3.03. Found: C, 39.58; H, 3.03.

percentage of color (hydrogen absorption), and the composition (derivatization of the cleavage products), may be determined with one sample which need not be greater than 10 g.

Acknowledgment.—A supply of water soluble sulfonated azo dyes, together with assays, was generously donated by Mr. Fred Hope. The assistance of Mr. Henry D. Lewis in making the carbon and hydrogen determinations is deeply appreciated.

Summary

The utility of the Raney nickel catalyst in the reduction of some common azo compounds at from 1–4 atmospheres absolute pressure and room temperature has been demonstrated.

BROOKLYN, N. Y. RECEIVED MAY 7, 1937

[CONTRIBUTION FROM THE LABORATORY OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA AGRICULTURAL EXPERIMENT STATION]

The Molecular Structure of Canna Starch

BY W. Z. HASSID AND W. H. DORE

The investigations of Haworth and collaborators[1-3] have shown that the structure of the starch molecule is a continuous unbranched chain of from 26 to 30 anhydroglucose units joined uniformly by α-glucosidic linkages between the first and fourth carbon atoms of contiguous hexose units. This structure has been shown to hold equally well for starch from potato, maize or waxy maize although these three starches have markedly different physical properties. It appears important to determine whether still other types of starch have the same molecular structure, hence the present contribution which reports the results of an investigation of starch obtained from the canna plant (*Canna edulis*).[4]

Canna starch is characterized by the large size of its granules, some of which are more than 0.1 mm. in diameter. Like potato starch it gives a blue color with iodine and is not soluble in either hot or cold water. It does not gelatinize as readily as potato starch. Its specific rotation in 4% sodium hydroxide solution is +156°, in reasonably good agreement with values obtained by Hirst, Plant and Wilkinson[2] for potato amylose (+151°) and amylopectin (+151°) and by Haworth, Hirst and Woolgar[3] for regenerated waxy maize starch (+152°), all of these determinations being made in either 4 or 5% sodium hydroxide solution. Canna starch is hydrolyzed at the same rate as potato starch and this suggests that the two have similar glucosidic linkages.

Canna starch was acetylated by two methods: (a) the method of Haworth, Hirst and Plant[5] using pyridine as a catalyst and (b) the method of Barnett[6] as modified by Irvine and Hirst[7] and by Haworth, Hirst and Webb[8] using chlorine and sulfur dioxide as catalysts. Both products had the full acetyl content for triacetyl starch. The starch which was regenerated from the acetate prepared by method (a) was insoluble in water and gave the same specific rotation (+156°) in 4% sodium hydroxide solution as the original starch. The starch, regenerated from the acetate which was prepared by method (b), was soluble in water but otherwise it was similar to the original canna starch in its properties. Its specific rotation in water solution was +198°, which is comparable with the value +190° reported for potato amylose[2] and +212° reported for waxy maize,[3] both in water solution.

The methylation of starch as carried out by the early investigators was very laborious, involving as many as forty treatments to complete the methylation. Later Irvine and Macdonald[9] improved this procedure by applying methyl sulfate and sodium hydroxide directly to the original starch and obtained trimethyl starch after twenty-four methylation treatments but in rather poor yield. Haworth, Hirst and Webb[8] reduced the number of treatments to six by employing a specially prepared triacetyl starch and methylating it in an acetone solution. After the first methylation

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(1) Haworth, *Ann. Rev. Biochem.*, **5**, 81 (1936).

(2) Hirst, Plant and Wilkinson, *J. Chem. Soc.*, 279 (1932).

(3) Haworth, Hirst and Woolgar, *ibid.*, 177 (1935).

(4) The canna starch was obtained through the courtesy of Professor R. S. Bean, University of Hawaii, Honolulu.

(5) Haworth, Hirst and Plant, *J. Chem. Soc.*, 1214 (1935).

(6) Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).

(7) Irvine and Hirst, *J. Chem. Soc.*, **121**, 1585 (1922); **125**, 15 (1924).

(8) Haworth, Hirst and Webb, *ibid.*, 2681 (1928).

(9) Irvine and Macdonald, *ibid.*, 1502 (1926).