

HYDROGENATION OF NITROAROMATICS IN THE PRESENCE OF THE NEW PLATINUM METAL AND CARBON-SUPPORTED PLATINUM METAL CATALYSTS

Sir:

The treatment of salts of the platinum metals with aqueous or ethanolic sodium borohydride, either in the presence or absence of decolorizing carbon, results in the immediate formation of intensely black, finely divided products, which exhibit high activity for the hydrolysis of borohydride and the hydrogenation of unsaturated hydrocarbons.<sup>1</sup> We wish to report that the combination of these active catalysts, conveniently formed *in situ*, with the ready availability of hydrogen generated *in situ* from sodium borohydride, permits the convenient hydrogenation of nitroaromatics in simple glass apparatus.

In order to investigate the relative effectiveness of the various platinum metals as catalysts, the apparatus and procedures utilized for the hydrogenation of olefins were modified slightly. The apparatus consisted of a 250-ml. Erlenmeyer flask fitted with a magnetic stirrer, a short manometer which permitted the escape of hydrogen at pressures of 25 mm. above atmospheric, an inlet port fitted with a rubber serum cap, and a 50-ml. buret. The flask was immersed in a water bath at 25°. In the flask was placed 40 ml. of anhydrous ethanol and 1.0 ml. of a 0.2 M solution of the platinum metal salt. The catalyst was generated by introducing 5.0 ml. of a 1.00 M solution of sodium borohydride in ethanol to the vigorously stirred solution. After one minute, 4.0 ml. of concentrated hydrochloric acid was injected with a hypodermic syringe to destroy the excess sodium borohydride and to provide a hydrogen atmosphere. (The increased quantity of hydrochloric acid is for the purpose of neutralizing the aniline as it is formed.) The reaction is initiated by injecting 2.05 ml., 20.0 mmoles, of nitrobenzene. In cases where the supported catalysts were examined, 1.0 g. of decolorizing carbon (Darco K-B) was introduced into the flask prior to reduction of the metal salt. The standard borohydride solution, 1.00 M in ethanol, was introduced from the buret at the rate required to maintain the pressure at atmospheric. Following completion of the fast, initial phase of the reaction, which utilized an amount of borohydride quantitatively equivalent to the reduction of the nitrobenzene to aniline, there was observed a much slower, secondary reaction, presumably involving reduction of the aromatic ring. Completion of the fast phase was taken as the reaction time. The results are summarized in Table I.

The results reveal that both in the unsupported and the carbon-supported forms, the most active catalysts for the hydrogenation of the nitro group are palladium and platinum. The carbon-support is highly beneficial, increasing the rate of the hydrogenation by a factor of approximately 4 to 5. A comparison with commercial samples of 5% palladium and platinum on charcoal revealed that the *in situ* prepared catalysts are approximately twice as active.

(1) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493, 1494, 1495, 2827 (1962).

TABLE I

HYDROGENATION OF NITROBENZENE AT 25° BY UNSUPPORTED AND CARBON-SUPPORTED PLATINUM METAL CATALYSTS PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Catalyst <sup>a</sup>	Unsupported catalyst		Carbon-supported catalyst	
	Time, min.	Reaction %	Time, min.	Reaction %
Ruthenium	60	3	60	3
Rhodium	60	25	60	85
Palladium	49	100	12	100
Osmium	60	6	60	6
Iridium	60	20	60	34
Platinum	46	100	10	100
Palladium/charcoal <sup>b</sup>			24	100
Platinum/charcoal <sup>b</sup>			23	100

<sup>a</sup> 0.2 mmole metal for 20 mmoles of nitrobenzene. <sup>b</sup> Commercial catalysts—5% metal on charcoal.

In order to examine the general applicability of this procedure for the conversion of nitroaromatics into amines, a number of representative compounds were reduced and the amine products isolated and identified. The results are summarized in Table II.

TABLE II

HYDROGENATION OF REPRESENTATIVE NITROAROMATICS AT 25° OVER THE CARBON-SUPPORTED PLATINUM CATALYST PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Compound <sup>a</sup>	M.p., °C.	Reacn. time, min.	Benzoyl derivative	Yield, %
Nitrobenzene		10	Aniline <sup>b</sup>	91
<i>p</i> -Nitrotoluene	51	9	<i>p</i> -Toluidine, m.p. 157	96
<i>p</i> -Nitroanisole	55	11	<i>p</i> -Anisidine, m.p. 154	88
<i>p</i> -Nitrophenol	112-113	13	<i>p</i> -Aminophenol, m.p. 234	83
1-Nitronaphthalene	56-57	12	1-Naphthylamine, m.p. 161	91
Ethyl <i>p</i> -nitrobenzoate	56	9	Ethyl <i>p</i> -aminobenzoate <sup>c</sup>	92
<i>p</i> -Chloronitrobenzene	83	8	<i>p</i> -Chloroaniline, m.p. 190	86

<sup>a</sup> 20 mmoles compound over 0.20 mmole platinum on 1.0 g. carbon (Darco K-B). <sup>b</sup> Isolated as aniline hydrochloride, m.p. 197°. <sup>c</sup> Isolated as the free amine, m.p. 90°.

It should be pointed out that the direct reduction of nitroaromatics by sodium borohydride in the presence of palladium-charcoal has been reported recently.<sup>2</sup> However, we have encountered difficulties in attempting to utilize this procedure on a scale suitable for normal preparative needs, whereas the hydrogenation procedure appears to be applicable without modification to syntheses on a relatively large scale. A particularly simple procedure for carrying out relatively large scale hydrogenations is described in the following Communication.<sup>3</sup>

We wish to acknowledge the generous assistance of Engelhard Industries, Inc., for samples of the various platinum metal salts utilized in this study.

RICHARD B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

HERBERT C. BROWN  
K. SIVASANKARAN

RECEIVED JUNE 14, 1962

(2) T. Neilson, H. C. S. Wood and A. G. Wylie, *J. Chem. Soc.*, 372 (1962).

(3) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).