Since the atomic weight of rhodium is one-half that of platinum, it is evident that on a weight basis rhodium is approximately twice as effective as the platinum catalyst and nearly four times as effective as the commercial platinic oxide catalyst.

The easy synthesis of the highly active platinum catalysts *in situ* makes unnecessary the hazardous introduction of the active platinum catalyst into the organic solvent.[3] Moreover, the high activity of the catalysts suggests the practicality of achieving laboratory scale hydrogenations in simple glass equipment, eliminating the need for pressure equipment.

Acknowledgment.—We wish to acknowledge the generous assistance of Engelhard Industries, Inc., for the samples of the various platinum metal salts.

[3] P. N. Rylander, *Engelhard Industries Technical Bulletin*, **1**, 93 (1960).

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY HERBERT C. BROWN
LAFAYETTE, INDIANA CHARLES A. BROWN

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A NEW CONVENIENT TECHNIQUE FOR THE HYDROGENATION OF UNSATURATED COMPOUNDS

Sir:

The treatment of salts of the platinum metals with aqueous sodium borohydride results in the formation of intensely black, finely divided products which exhibit high activity for catalytic hydrogenation.[1,2] The combination of these new active catalysts, conveniently formed *in situ*, with the ready availability of hydrogen, generated *in situ* from sodium borohydride, makes possible the convenient hydrogenation of unsaturated compounds on a preparative scale in simple glass apparatus.

The apparatus consisted of a 100-ml. round-bottom flask fitted with a magnetic stirrer, a short manometer which allowed the escape of hydrogen at pressures of 25 mm. above atmospheric, an inlet port fitted with a rubber serum cap, and a graduated dropping funnel. (A 50-ml. buret was commonly used for greater accuracy.) The flask was usually immersed in a 25° constant temperature bath, although this refinement is not necessary for preparative work.

A standard stabilized solution (1.00 *M*) of sodium borohydride in ethanol was prepared by dissolving 3.8 g. (100% basis) of sodium borohydride in 100 ml. of a solvent prepared by adding anhydrous ethanol to 5 ml. of 2.00 *M* aqueous sodium hydroxide. In the hydrogenation flask was placed 1.0 ml. of 0.2 *M* chloroplatinic acid[3] and 40 ml. of anhydrous ethanol. The apparatus was briefly flushed with nitrogen, and 5.0 ml. of the standard sodium borohydride solution was added rapidly to the vigorously stirred solution of chloroplatinic acid. There was an immediate formation of the jet black catalyst suspension. After approximately 1 minute, 4.0 ml. of 6 *M* hydrochloric acid was injected, destroying the excess borohydride and providing a hydrogen atmosphere. The reaction was initiated by injecting 40 mmoles of the olefin. The standard borohydride solution then was added from the dropping funnel at such a rate as to maintain the pressure in the flask at approximately atmospheric.

The reaction proceeded at a rate considerably more rapid than the corresponding reaction involving hydrogen supplied from an external source. For example, the hydrogenation of 1-octene is complete in 9–10 minutes, as compared to the 16–18 minutes required in the earlier procedure.[2] The reaction time of 9–10 minutes proved to be readily reproducible in successive runs.

min.	ml.	$NaBH_4$ %	min.	ml.	$NaBH_4$ %
0	0.0	0	6	6.0	60
1	1.0	10	7	6.9	69
2	2.0	20	8	7.9	79
3	3.0	30	9	8.9	89
4	4.0	40	10	9.9	99
5	5.0	50	15	9.9	99

It should be noted that this reaction time of 10 minutes compares with a reaction time of 27 minutes for the same reduction utilizing commercial platinic oxide catalyst and an external hydrogen source.[2]

Representative unsaturated compounds were hydrogenated in order to test the sensitivity of the procedure to the olefin structure. However, with the exception of cycloöctene, which required 88 minutes for complete hydrogenation, all of the compounds examined underwent quite rapid hydrogenation: 1-octene, 10 min.; 2-octene, 14 min.; 2,4,4-trimethyl-1-pentene, 18 min.; cyclohexene, 15 min.; cycloöctene, 88 min.; norbornene, 8 min.; 4-vinylcyclohexene (20 mmoles), 12.5 min.; 3-hexyne (20 mmoles), 14 min. Under the same conditions, benzene (16.7 mmoles) underwent hydrogenation slowly—approximately 16% in 1 hour.

It is interesting that the rates of hydrogenation appear to parallel closely the heats of hydrogenation of these olefins.[4] This development would also appear to have utility in analytical chemistry, since it has been possible to estimate the olefin introduced from the volume of borohydride utilized with an accuracy of 1%. Finally, we have considerably increased the quantity of material hydrogenated merely by utilizing larger apparatus and a mechanically driven stirrer. Consequently, this procedure should permit laboratory hydrogenations on a significant preparative scale.

We are exploring the utilitity of the different platinum metal catalysts for selective hydrogenations.

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

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY HERBERT C. BROWN
LAFAYETTE, INDIANA CHARLES A. BROWN

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[1] H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493 (1962).

[2] H. C. Brown and C. A. Brown, *ibid.*, **84**, 1494 (1962).

[3] The commercially available 10% chloroplatinic acid solutions are approximately 0.2 *M*.

[4] R. B. Turner, "Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, pp. 67–83.