

we observed that many of these also exert a powerful catalytic effect on the hydrolysis of borohydride. The platinum family metals proved to be unusually effective and were subjected to a detailed study.

TABLE I
TIME REQUIRED FOR LIBERATION OF ONE-HALF OF THE AVAILABLE HYDROGEN FROM AQUEOUS SODIUM BOROHYDRIDE

Metal	Compound used	Time, min.
Iron	FeCl ₂	38
Cobalt	CoCl ₂	9
Nickel	NiCl ₂	18
Ruthenium	RuCl ₃	0.3
Rhodium	RhCl ₃	0.3
Palladium	PdCl ₂	180
Osmium	OsO ₄	18.5
Iridium	IrCl ₄	28
Platinum	H ₂ PtCl ₆	1

The following procedure was utilized. A stirred solution of 1.00 g. of sodium borohydride in 45.0 ml. of water in a 125 ml. erlenmeyer flask was maintained in a constant temperature bath at 25°. Reaction was initiated by injecting 5.0 ml. of a 0.100 M solution of the appropriate metal salt with a hypodermic syringe. The salt was instantly reduced with the formation of a deep black, finely-divided solid. The hydrogen evolved was passed through a wet-test meter, and the volume realized at regular intervals of time was noted. The results are summarized in Table I.

It is evident that the effectiveness of osmium and iridium is modest, approximating the previously known activities of iron, cobalt and nickel. Moreover, palladium exhibits much poorer catalytic activity. However, platinum is a highly effective catalyst, with a half-life approximately one-tenth that of cobalt, and both ruthenium and rhodium are even more active catalysts. In these last cases, the activities are so high that the half-lives can only be considered to be approximate—the solutions evolve hydrogen almost explosively with the injection of the metal salt solution.

The black powder produced by treating chloroplatinic acid with sodium borohydride was isolated and analyzed. It was essentially pure platinum. Consequently, it appears that sodium borohydride reduces these platinum metals to the elementary state, in a form which exhibits high catalytic activity for the hydrolysis reaction.

We are exploring the catalytic activity of these products for other reactions.

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A SIMPLE PREPARATION OF HIGHLY ACTIVE PLATINUM METAL CATALYSTS FOR CATALYTIC HYDROGENATION

Sir:

The treatment of platinum metal salts with aqueous sodium borohydride results in the immediate formation of finely-divided black precipitates which are active catalysts for the hydrolysis

of sodium borohydride.¹ We wish to report that these materials are also highly active catalysts for the hydrogenation of typical olefins, such as 1-octene. Indeed, the platinum catalyst obtained by this simple procedure exhibits an activity of nearly 100 per cent. greater than that of commercial platonic oxide (Adams catalyst²) now widely used for laboratory hydrogenation, and the rhodium catalyst realized in this procedure is even more active.

The apparatus utilized for following the rates of hydrogenation of 1-octene consisted of a 100-ml. round-bottom flask, fitted with a magnetic stirrer, an inlet for hydrogen, an outlet leading to a short manometer, and an injection port fitted with a rubber serum cap. The flask was immersed in a 25° constant temperature bath. Hydrogen was conveniently generated in an adjacent flask by adding a 1.00 M solution of sodium borohydride in a buret to aqueous acid. In the hydrogenation flask was placed 1.0 ml. of 0.20 M chloroplatinic acid, then 40 ml. of anhydrous ethanol. The flask was briefly flushed with nitrogen. The catalyst was generated *in situ* by injecting 5.0 ml. of a 1.00 M solution of sodium borohydride in ethanol. The excess borohydride was destroyed and a hydrogen atmosphere achieved by injecting 4.0 ml. of 6 M hydrochloric acid. The 1-octene, 40 mmoles, was injected into the vigorously stirred solution. Hydrogen absorption began immediately. The standard solution of sodium borohydride was added to the generating flask (previously flushed with hydrogen) at such a rate as to maintain the pressure in the apparatus at approximately atmospheric. The results reveal an essentially linear absorption of hydrogen, complete in 16 to 18 minutes.

min.	%	min.	%
0	0	10	68
2.0	10	12	80
4.0	21	14	92
6.0	31	16	98
8.0	43	18	100

Under identical conditions, the reaction utilizing commercial platonic oxide was complete in 26 to 28 minutes.

Table I summarizes the results realized with the various platinum metal catalysts.

TABLE I
RATES OF HYDROGENATION OF 1-OCTENE BY VARIOUS PLATINUM METAL CATALYSTS PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Metal ^a	Compound used	Time, min. ^b	
		50%	100%
Ruthenium	RuCl ₃	70	(170)
Rhodium	RhCl ₃	7	20
Palladium	PdCl ₂	16	(90)
Osmium	OsO ₄	45	(110)
Iridium	IrCl ₄	32	(80)
Platinum	H ₂ PtCl ₆	9	17
(Platinic oxide)	PtO ₂	14	27

^a 0.2 mmole for 40 mmoles of 1-octene. ^b Values in parentheses are estimated times for complete reaction.

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

(2) R. Adams and R. L. Shriner, *ibid.*, **45**, 2171 (1923).

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 platinum 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).

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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 acid³ 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 platinum 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 cyclooctene, 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.; cyclooctene, 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 utility of the different platinum metal catalysts for selective hydrogenations.

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

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(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.