COMMUNICATIONS TO THE EDITOR

REACTION OF SODIUM BOROHYDRIDE WITH PLATINUM METAL SALTS IN THE PRESENCE OF DECOLORIZING CARBON—A SUPPORTED PLATINUM CATALYST OF MARKEDLY ENHANCED ACTIVITY FOR HYDROGENATIONS

Sir:

We previously reported that the treatment of platinum metal salts with aqueous or ethanolic sodium borohydride results in the immediate formation of finely-divided black precipitates which are active catalysts both for the hydrolysis of sodium borohydride[1] and for the hydrogenation of unsaturated compounds.[2] We now wish to report that the reduction of platinum metal salts in the presence of decolorizing carbon produces rhodium, palladium and platinum catalysts of markedly enhanced activities.

The apparatus was modified slightly from that previously utilized to follow rates of hydrogenations.[3] It consisted of a 125-ml. Erlenmeyer 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 25-ml. buret. The flask was immersed in a water bath at 25°. In the flask was placed 1.0 g. of decolorizing carbon (Darco K-B), followed by 40 ml. of anhydrous ethanol and 1.0 ml. of a 0.2 *M* solution of the platinum metal salt. The supported catalyst was generated *in situ* by injecting 5.0 ml. of a 1.00 *M* solution of sodium borohydride in ethanol. After approximately one minute, 4.0 ml. of 6 *M* hydrochloric acid was introduced to destroy excess borohydride and to generate a hydrogen atmosphere. The reaction was initiated by injecting with a hypodermic syringe 6.3 ml. (40 mmoles) of 1-octene into the vigorously stirred solution. Hydrogen absorption began immediately. The standard solution of sodium borohydride was added to the reaction flask at such a rate as to maintain the pressure in the apparatus at approximately atmospheric. The results are summarized in Table I.

TABLE I

HYDROGENATION OF 1-OCTENE AT 25° OVER UNSUPPORTED AND CARBON-SUPPORTED PLATINUM METAL CATALYSTS PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Catalyst[a]	Unsupported catalyst 50% Time, min.	Unsupported catalyst 100% Time, min.	Carbon-supported catalyst 50% Time, min.	Carbon-supported catalyst 100% Time, min.
Ruthenium	54	(150)[b]	Slow[c]	
Rhodium	5	11	3	5.5
Palladium	8	28	2.5	5
Osmium	55	(165)[b]	Slow[d]	
Iridium	75	(170)[b]	Slow[e]	
Platinum	6	11	2	4
Platinum oxide[f]	13	27		
Platinum/charcoal[f]			6	16

[a] 0.2 mmole metal for 40 mmoles of 1-octene. [b] Values in parentheses are estimated time for complete reaction. [c] 40% in 60 min. [d] 7% in 60 min. [e] 3% in 60 min. [f] Commercial catalysts. External hydrogen.

It is noteworthy that the three platinum metals which exhibit the highest activity for the hydrogenation, namely, rhodium, palladium and platinum, all exhibit markedly enhanced activities with the carbon support. On the other hand, the other three metals, ruthenium, osmium and iridium, actually exhibit a decreased catalytic effectiveness in the presence of the support.

The carbon-supported platinum catalyst was selected for further study. A number of representative unsaturated hydrocarbons were hydrogenated by the above procedure and the results compared with those realized by use of the unsupported catalyst. The results are summarized in Table II.

TABLE II

HYDROGENATION OF REPRESENTATIVE UNSATURATED HYDROCARBONS AT 25° OVER UNSUPPORTED AND CARBON-SUPPORTED PLATINUM CATALYSTS PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Compound[a]	Unsupported platinum[d] Time, min.	Carbon-supported platinum[e] Time, min.
1-Octene	11	4
Cyclopentene	23	6.5
Cyclohexene	15	5.5
Cycloheptene	19	7
Cycloöctene	88, 64	15
1-Methylcyclohexene	32	7
1,2-Dimethylcyclohexene	75	24
4-Vinylcyclohexene[b]	12.5	6
3-Hexyne[b]	14	6.5
Benzene[c]	20% in 1 hr.	32% in 1 hr.

[a] 40 mmole, except where otherwise indicated. [b] 20 mmole. [c] 13.3 mmole. [d] 0.20 mmole. [e] 0.20 mmole on 1.0 g. carbon (Darco K-B).

It is evident that the carbon-supported catalyst increases the rate of hydrogenation of these representative unsaturated hydrocarbons by approximately 200 to 400% over the rates realized with the unsupported catalyst. It was previously pointed out that this unsupported catalyst, produced *in situ* by borohydride reduction, is itself considerably more active than the commonly utilized platinum oxide catalyst. Both the high activities of these new catalysts and their simple, convenient formation *in situ* suggest that they should prove very useful in facilitating hydrogenations in the laboratory, particularly in cases where a reasonable rate is desired at atmospheric pressures.

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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RECEIVED JUNE 14, 1962

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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) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1495 (1962).